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*Janet Szot*  
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

US PATENT APPLICATION PUBLICATION: 2004/0191198A1

PUBLICATION DATE: September 30, 2004 *OK*

SERIAL NUMBER: 10/810,671 *to enter*

FILING DATE: March 29, 2004

APPLICANT: Veronika Hochstein et al. *Mari*

APPLICANT ATTY. DOCKET: Merck-2867 *SEARCHED*  
*TECH* *12/13/04*

TITLE: Pigment Mixture and the Use Thereof in Cosmetics and in the Foods and Pharmaceuticals Sector

Commissioner of Patents  
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Dear Sir:

THIRD PARTY SUBMISSION UNDER 37 CFR §1.99

The undersigned hereby files a third party submission in the above-identified US patent application published on September 30, 2004. This submission is filed within two months of said publication. According to the [www.uspto.gov](http://www.uspto.gov)'s PAIRS, a notice of allowance has not been mailed in the above-identified US patent application publication.

Please charge the \$180.00 fee set forth in 37 CFR §1.17(p) to Deposit Account 05-1070.

12/02/2004 EAREGAY1 00000056 051070 10810671

01 FC:1806 180.00 DA

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A list of the enclosed documents including the publication date follows:  
Engelhard Chameleon Galaxy Plum Nail Enamel brochure published 2000;  
Engelhard Styling Gel publication brochure published 2000;  
Japanese Patent Publication 11340 published January 16, 2001 (English translation  
is enclosed.)

Engelhard Smokes and Sparkles Body Powder Misty Taupe brochure published  
2002;

IP.com posting published February 6, 2002;

WO 02/090448A2 published November 14, 2002; and

WO 03/006558A2 published January 23, 2003.

This submission is also being served under 37 CFR § 1.248 on Applicant at its  
correspondence address: John A. Sopp, Millen, White, Zelano, and Branigan, 2200  
Clarendon Boulevard, Suite 1400, Arlington, Virginia 22201.

Respectfully submitted,

Melanie L. Brown  
Melanie L. Brown  
Reg. No. 31,592

Enclosures

Engelhard Corporation  
101 Wood Avenue  
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(732) 205-5181



3

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**CHAMELEON**  
**Galaxy Plum Nail Enamel**  
**CLN-000074D**

**INGREDIENTS**

% WT

Suspending Lacquer SLF-2 (Butyl Acetate (and) Toluene (and) Nitrocellulose (and) Tosylamide/Formaldehyde Resin (and) Isopropyl Alcohol (and) Dibutyl Phthalate (and) Ethyl Acetate (and) Camphor (and) n-Butyl Alcohol (and) Silica (and) Quaternium-18 Hectorite) <sup>1</sup>	82.00
Desert Reflections™ Painted Desert Plum 663Z (Mica (and) Titanium Dioxide (and) Iron Oxides) <sup>1</sup>	3.50
Reflecks™ Beams of Blue G630L (Calcium Sodium Borosilicate (and) Titanium Dioxide) <sup>1</sup>	2.00
Lacquer 127P ( Butyl Acetate (and) Toluene (and) Nitrocellulose (and) Tosylamide/Formaldehyde Resin (and) Isopropyl Alcohol (and) Dibutyl Phthalate (and) Ethyl Acetate (and) Camphor (and) n-Butyl Alcohol) <sup>1</sup>	<u>12.50</u>
	100.00

**PROCEDURE:**

Combine all the components in an appropriate size vessel fitted with a Lightnin™ type propeller mixer. Continue mixing until batch is uniform.

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# **Styling Gel**

## **CLH-003014**

<b>PHASE</b>	<b>INGREDIENTS</b>		<b>% WT.</b>
A.	Water Carbomer (Carbopol Ultrez 10) <sup>1</sup>	(q.s. to 100%)	72.10 0.60
B.	Methylpropanediol (MP Diol) <sup>2</sup> Preservatives		3.00 q.s.
C.	Triethanolamine (99%) Water		0.50 2.00
D.	Water PVP (PVP K-30) <sup>3</sup> Disodium EDTA		10.00 0.15 0.05
E.	Polysorbate 80 (Tween 80) <sup>4</sup> <b>Cellini® Yellow 220CY5S</b> (Mica (and) Titanium Dioxide (and) Yellow 5 Lake (and) Hydrogenated Polyisobutene (and) Palmitic Acid) <sup>5</sup> <b>Cellini® Coral 420CR40F</b> (Mica (and) Titanium Dioxide (and) Red 40 Lake (and) Hydrogenated Polyisobutene (and) Palmitic Acid) <sup>5</sup> <b>Reflecks™ Gleams of Gold G230L</b> (Calcium Sodium Borosilicate (and) Titanium Dioxide) <sup>5</sup> Water Benzophenone-4 (Escalol 577) <sup>3</sup>		1.90 0.10 0.20 0.15 9.00 0.05
F.	Fragrance (18567H) <sup>6</sup> Polysorbate 80 (Tween 80) <sup>4</sup>		0.10 0.10 100.00

**NOTE: Do not use in the area of the eye.**

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## **PROCEDURE**

- I. Combine Phase A ingredients and mix slowly until thoroughly dispersed.
- II. Add pre-mixed Phase B to Phase A while mixing until completely uniform.
- III. Add Phase C to Phase A-B while under agitation.
- IV. Pre-mix Phase D ingredients until PVP is dissolved and add to Phase A-B-C.
- V. Pre-disperse pigments in Polysorbate 80 (Phase E), add water and Benzophenone-4. Mix until uniform and add to the batch with continuous mixing.
- V. Pre-mix Phase F ingredients, add to the batch and mix until uniform.

## **SUPPLIERS**

1. Noveon, Inc.
2. Lyondell Chemical Company
3. ISP
4. Uniqema
5. **Engelhard Corporation**
6. Shaw Mudge & Company

**CLH-003014**

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**SMOKES & SPARKLES**  
Body Powder  
*Misty Taupe*  
CLB-020108

Phase	Ingredients	% wt.
A.	Mearlcite™ SRA (Mica (and) Lauroyl Lysine) <sup>1</sup>	(q.s. to 100%)
	Magnesium Myristate	2.90
	Silk Powder (Crosilk Powder) <sup>2</sup>	3.90
	Boron Nitride	1.90
	Timica® Nu-Antique Silver 110AB (Mica (and)	
	Titanium Dioxide (and) Iron Oxides) <sup>1</sup>	5.00
	Preservatives	q.s.
B.	Caprylic/Capric Triglyceride (Neobee M-5) <sup>3</sup>	4.25
	Phenyl Trimethicone (Dow Corning 556 Fluid) <sup>4</sup>	3.25
	Tocopheryl Acetate	1.00
	Fragrance	q.s.
C.	Reflecks™ Really Rouge G670L (Calcium Sodium	
	Borosilicate (and) Iron Oxides) <sup>1</sup>	3.00
	Reflecks™ Glimmers of Green G830L (Calcium Sodium	
	Borosilicate (and) Titanium Dioxide) <sup>1</sup>	22.00
		100.00

## **PROCEDURE:**

- I. Thoroughly blend and disperse Phase A in appropriate dry blending/dispersing equipment.
  - II. Spray pre-mixed Phase B into Phase A.
  - III. Add Phase C to Phase A-B and mix with low shear agitation until uniform.

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2. Croda, Inc.
3. Stepan Company
4. Dow Corning Corporation

**CLB-020108**

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特開2001-11340

(P2001-11340A)

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審査請求 未請求 請求項の数 3 O L (全 12 頁) 最終頁に続く

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最終頁に続く

(54) 【発明の名称】 真珠光沢顔料およびそれを配合した化粧料

(57) 【要約】

【課題】 化粧料に配合した場合に、くすみがなく、非常に良好な光輝性を発現し、肌上でのざらつき感がなく、のびおよびフィット感に優れる安価な真珠光沢顔料、さらにはそれを配合する光輝感に優れた化粧料を提供する。

【解決手段】 シリカ ( $SiO_2$ ) を45～75重量%含有し、平均厚さ0.1～2.5  $\mu m$ 、平均粒径1～300  $\mu m$ 、アスペクト比10～500のガラスフレークを熔融法により製造する。アスペクト比とは、平均粒径を平均厚さで除した値 (平均粒径/平均厚さ) をいう。

## 【特許請求の範囲】

【請求項1】 母材がシリカ( $\text{SiO}_2$ )を45～75重量%含有し、平均厚さが0.1～2.5μm、平均粒径が1～300μm、アスペクト比が10～500である真珠光沢顔料。

【請求項2】 上記母材の表面に貴金属およびチタニアが付着した請求項1に記載の真珠光沢顔料。

【請求項3】 請求項1または2に記載の真珠光沢顔料を配合した化粧料。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】この発明は、母材の組成、厚さ、粒径およびアスペクト比が一定範囲にある真珠光沢を有する顔料およびその顔料を配合した化粧料に関する。さらには、前記真珠光沢顔料が金属酸化物の被膜を備えたガラスフレークであるものに関する。

## 【0002】

【従来の技術】真珠光沢を示す光輝性薄片状粉体として、天然や合成の雲母(マイカ)を母材とし、その表面に酸化チタンや酸化鉄などをコーティングしたいわゆるパールマイカが従来から知られている。しかし、マイカは劈開性があるため、その表面に段差ができ易く、表面平滑性が十分でない場合が多い。そのため、マイカを母材とした真珠光沢顔料は良好な光輝感を発現するとは言い難い。また、天然雲母には不純物が多く含まれることから、これを母材とする真珠光沢顔料は、化粧料に配合された場合にくすみの原因となる。

【0003】真珠光沢顔料としては、特開平9-176515号公報に、平均形状比(平均厚さ/平均粒度)1/9～1、粒度25～500μmの金属酸化物コーティングフレーク状粉体が記載されている。このフレーク状粉体は、化粧料材料に使用された場合、計算上その厚さが2.78μm以上となることから、肌上でざらざら感を与え、また平均形状比が大きく立方体に近い形状のため、肌上でののびまたはフィット感が悪く、さらに同重量の薄いフレークに比べて枚数が少なくなるため、反射による光輝感が少ないなどの問題がある。

【0004】また、特開平6-116507号公報には、金属アルコキシドから製造したフレーク状シリカガラスを母材とし、チタニアまたはジルコニアをコーティングした真珠光沢顔料が記載されている。このフレーク状シリカガラスは、金属アルコキシドが非常に高価であることからコスト上の問題がある。また、シリカガラスは通常のガラスと比較してシリカ含有率が高く硬度が高いため、化粧料材料に用いられた場合、材料配合工程で練り込まれる際に破碎され、その粒度が保てなくなるおそれが高い。粒度が小さくなるほど化粧料中に均一に分散され易くなる利点はあるが、一方で真珠光沢顔料との光輝感を発現し難くなるなどの問題がある。

【0005】さらに、特開昭62-187770号公報

には、ガラスフレークに微粒子酸化チタンをコーティングしてなる紫外線遮へい顔料が記載されている。しかし、この紫外線遮へい顔料は、真珠光沢感が事実上発現しない量の酸化チタンをコーティングするものである。

## 【0006】

【発明が解決しようとする課題】上述のように真珠光沢顔料を化粧品に配合することは従来から広く行われているが、天然または合成のマイカを母材とする真珠光沢顔料は、その不十分な表面平滑性のために、良好な光輝感を発現するとは言い難い面がある。また、天然雲母を母材とする場合では、不純物が含まれているため、化粧料に配合した場合、くすみの原因となる。さらに、フレーク状シリカガラスを母材とする場合では、コスト面および粒度が維持できない問題がある。

【0007】この発明は、このような従来技術に存在する問題に着目してなされたものである。その目的とするところは、化粧料に配合した場合に、くすみがなく、非常に良好な光輝性を発現し、肌上でのざらつき感がなく、のびおよびフィット感に優れる安価な真珠光沢顔料を提供することにある。さらには、のびがよく、フィット感に優れ、ざらつき感を生じることのない、光輝感に優れた化粧料を提供することにある。

## 【0008】

【課題を解決するための手段】上記目的を達成するため、請求項1に記載の発明の真珠光沢顔料は、母材がシリカ( $\text{SiO}_2$ )を45～75重量%含有し、平均厚さ0.1～2.5μm、平均粒径1～300μm、アスペクト比10～500であるものである。なお、前記アスペクト比とは、平均粒径を平均厚さで除した値(平均粒径/平均厚さ)をいう。

【0009】請求項2に記載の発明の真珠光沢顔料は、請求項1に記載の発明において、母材の表面に貴金属およびチタニアが付着したものである。

【0010】請求項3に記載の発明の化粧料は、請求項1または2に記載の真珠光沢顔料を配合したものである。

## 【0011】

【発明の実施の形態】以下、この発明の実施形態について詳細に説明する。この発明の真珠光沢顔料は、母材がシリカ( $\text{SiO}_2$ )を45～75重量%含有するものである。この母材としては、熔融法で製造されるガラスフレークが挙げられる。ガラスフレークは、公知の技術、たとえば特公昭41-17148号公報、特公昭45-3541号公報に記載の方法で製造することができる。すなわち、熔融したガラスを円型スリットから押し出し、そのガラスの内部に空気などを注入して中空状の円筒に膨らませ薄く均一なガラスフィルムとし、それを粉碎する方法で製造される。このガラスフレークは、安価な原料を熔融して製造するため、コストを低く抑えることができる。また、自由表面を持つ熔融ガラスを冷却固化するた

め、その表面は非常に平滑である。さらに、非晶質で劈開性を有しないので、その表面に段差が生じない。また、シリカが80重量%以上含有されるシリカガラスに比べ若干の柔軟性を有するため、化粧料に配合されても破碎され難く、配合時の粒度を保つことができる。ガラスとしては、熔融成形できるものならどのような組成でもよいが、一般に使われているソーダライムガラス、Cガラス、Eガラスなどが例示される。これらガラスは、シリカを上記範囲で含有するものである。

【0012】また、平均厚さ0.1~2.5μmのガラスフィルムを粉碎分級することにより、平均粒径1~300μm、アスペクト比10~50のガラスフレークが製造される。ガラスフレークは、製造技術上0.1μmより薄くできず、一方2.5μmより厚い場合、それが配合された化粧料にざらつき感を生じさせ、かつ光輝感を低下させる。アスペクト比が10より小さい場合は、配合された化粧料の肌でのびのびおよびフィット感を悪化させ、一方500より大きい場合は、その化粧料の肌へののりを悪化させ、ぎらぎら感を強く過ぎる。その平均粒径が1μm未満の場合は、配合された化粧料に十分な光輝感を付与することができず、一方300μmより大きい場合は、配合された化粧料において粒子が目立ち過ぎ、仕上がり感を不自然なものにしてしまう。

【0013】母材の形状が上記範囲にある場合、その母材のシリカの含有率によって、ガラスフレークの性質が異なる。シリカの含有率が75重量%より高くなると、熔融法による生産が困難になり、ゾルゲル法による生産が実際上主となる。シリカの含有率が高く、ゾルゲル法で製造されるガラスを以下「シリカガラス」と称するが、形状が上記範囲にあるシリカガラスのフレークは、上述の如く硬度が高くかつ脆いため、一定以上の外力が

加わると容易に破碎される。たとえば、シリカガラスのフレークに超音波を照射すると、その平均粒径が小さくなることが確認される。具体的には、超音波照射装置付きレーザー回折粒度分布測定装置（セイシン企業社製Pro7000S）を65Wで1分間出力させ、シリカガラスのフレークに超音波を照射すると、その平均粒径は下記「表1」のように変化する。

## 【0014】

## 【表1】

シリカガラスのフレークに超音波を照射した場合の粒径の変化

項目	初期平均粒径(μm)	超音波照射後(μm)
サンプル1	8.02	5.90
サンプル2	9.36	9.20
サンプル3	15.62	15.40
サンプル4	24.49	21.79
サンプル5	25.93	23.30
サンプル6	26.69	25.13
サンプル7	28.41	23.19
サンプル8	50.19	35.58
サンプル9	55.50	38.48
サンプル10	58.83	39.04

注)サンプル1~10には、SGシリーズ(日本板硝子社製)を用いた。

【0015】また、超音波の照射時間が増加するにしたがって、シリカガラスのフレークの平均粒径は小さくなることが確認される。具体的には、超音波洗浄装置（ヴェルヴォクーリア商會社製 VS-70R）を60Wで出力させ、シリカガラスのフレークに超音波を照射すると、その平均粒径は経時に下記「表2」のように変化する。

## 【0016】

## 【表2】

シリカガラスのフレークに超音波を照射した場合の粒径の経時的变化

項目＼照射時間	0min	0.5min	1min	2min	5min
サンプル1(μm)	23.19	14.70	13.63	12.35	11.25
サンプル2(μm)	69.08	37.79	34.30	30.74	27.89
サンプル3(μm)	183.80	85.73	67.70	60.04	56.05

注)サンプル1~3には、SGシリーズ(日本板硝子社製)を用いた

【0017】「表1」および「表2」より、シリカガラスのフレークは、粒径が大きいほど超音波による破碎が起こり易いことが判る。また、経的には、超音波照射の初期に破碎が起こり易いことが判る。このようにシリカガラスのフレークは、超音波の衝撃によっても破碎されてしまうが、ガラスフレークではこのような現象は確認されない。これは、ガラスフレークがシリカガラスのフレークほど硬度が高くなく若干の柔軟性を有するためであると考えられる。したがって、ガラスフレークを母材とする真珠光沢顔料は、化粧料の材料として他の材料と配合され練り込まれた場合に、シリカガラスのフレークよりも当初の粒径を維持でき、その結果化粧料中でより効果的に光輝感を発現できる。なお、ガラスフレーク

のシリカの含有率は、母材に必要な強度と適度な柔軟性とを兼ね備えるために、50~70重量%、さらには55~65重量%であることが好ましい。

【0018】この真珠光沢顔料は、その名の如く外観上真珠に似た光沢を示すものであり、これはガラスフレークにチタニア(TiO<sub>2</sub>)、ジルコニアまたは酸化鉄などの金属酸化物からなる被膜を設けることにより得られる。この被膜の成形方法は、公知の技術を利用すればよく、たとえば特公昭43-25644号公報、特開昭47-34529号公報に記載されている。具体的には、硫酸チタニル溶液または四塩化チタン溶液にガラスフレークを懸濁させ、かかる溶液を昇温することによりチタニアを析出させ、ガラスフレーク上に被膜を設ける方法であ

る。ただし、この方法に限定するものではなく、ガラスフレーク上に薄く被膜を設けることができる方法であれば、どのような方法でもよい。

【0019】ガラスフレーク上の被膜の厚さを制御することにより、干渉による任意の色調を発現させることができる。この被膜の厚さは、20~250nmが好ましく、20nm未満では光輝感が発現し難く、一方250nmより厚ければ原料が多く必要となるためコスト的に好ましくない。

【0020】この被膜にチタニアを用いる場合は、被膜形成後にガラスフレークを800~1,200°Cで加熱処理することが多い。これは、チタニアにはアナース型、ブルーカイト型およびルチル型の3つの結晶系があり、アナース型をルチル型に転移させるために行われるものである。上述のように溶液からの析出によりチタニア被膜を設ける場合は、まずアナース型が析出する。アナース型はルチル型に比べ化学的に不安定型であるため、ガラスフレークに耐久性および耐候性が要求される場合は、アナース型よりルチル型が指向される。さらに、ルチル型のチタニア被膜は、アナース型よりも緻密な膜を形成することから、より高い光輝感すなわち鮮やかな色感を発現する。よって、ガラスフレークの被膜としては、ルチル型のチタニアからなるものが好ましく、また指向されている。

【0021】上記結晶系転移のための加熱処理温度が800°C以下の場合は、チタニアの結晶系はアナース型のままであるが、一方800°Cより高くするとルチル型に転移することが知られている。しかし、800°C以上に加熱した場合、ガラスフレークは変形することがある。この変形を防止するため、本発明者は、800°C以下の加熱処理でもルチル型に転移する方法を、鋭意研究の末見出した。それは、上記の溶液からチタニアを析出させる際に、ガラスフレークに貴金属を微量触媒として付着させておく方法である。ここで貴金属とは、金、銀および白金族(Ru, Rh, Pd, Os, Ir, Pt)を指す。貴金属をガラスフレークに付着させる方法は、とくに限定されるものではなく、たとえば塩化白金酸の溶液中にガラスフレークを投入してしばらく放置する方法が挙げられる。この方法において、600°C以下の加熱処理でルチル型への結晶系転移が起こることを確認した。

【0022】ガラスフレーク上の被膜の屈折率によって、ある色調を発現させる被膜の厚さは若干異なるが、一般的には被膜の厚さと発色(反射光)の関係は以下の「表3」とおりである。

【0023】

【表3】

発色	被膜厚さ (nm)
シルバー	40~60
黄	60~80
赤	80~100
青	100~140
緑	120~160

【0024】上記金属酸化物の被膜を備えた特定の形状のガラスフレークすなわち真珠光沢顔料を配合することにより、くすみがなく澄んだ発色を示し、肌上でざらつき感がなく、さらに肌上でののびおよびフィット感に優れる化粧料が得られる。

【0025】この化粧料における真珠光沢顔料の配合率は、1~100重量%が好ましい。配合率が1重量%未満の場合は、真珠光沢顔料の光輝感が十分に発揮されない。一方、100重量%であっても、肌上では人脂などが存在するため、これらと結合し化粧料として機能しうる。

【0026】この化粧料には、フェーシャル化粧料、メーキャップ化粧料、ヘア化粧料など幅広い範囲の化粧料が含まれる。これらの中でも、とくにファンデーション、粉白粉、アイシャドー、ブラッシャー、化粧下地、ネイルエナメル、アイライナー、マスカラ、口紅、ファンシーパウダーなどのメーキャップ化粧料において、この真珠光沢顔料は好適に使用される。

【0027】この真珠光沢顔料は、化粧料の目的に応じて、適宜疎水化処理が施されてもよい。疎水化処理の方法としては、第一にメチルハイドロジエンポリシロキサン、高粘度シリコーンオイルおよびシリコーン樹脂などのシリコーン化合物による処理方法、第二にアニオン活性剤、カチオン活性剤などの界面活性剤による処理方法、第三にナイロン、ポリメチルメタクリレート、ポリエチレン、テフロン、ポリアミノ酸などの高分子化合物による処理方法、第四にパーカルオロ基含有化合物、レシチン、コラーゲン、金属石鹼、親油性ワックス、多価アルコール部分エステルまたは完全エステルなどによる処理方法、第五にこれらを複合した処理方法が挙げられる。ただし、一般に粉末の疎水化処理に適用できる方法であれば、上記の方法に限定されるのではない。

【0028】この化粧料には、通常化粧料に用いられる他の材料を必要に応じて適宜配合することができる。たとえば、タルク、カオリソ、セリサイト、白雲母、金雲母、紅雲母、黒雲母、リチア雲母、バーミキュライト、炭酸マグネシウム、炭酸カルシウム、珪藻土、ケイ酸マグネシウム、ケイ酸カルシウム、ケイ酸アルミニウム、ケイ酸バリウム、硫酸バリウム、ケイ酸ストロンチウム、タンゲステン酸金属塩、シリカ、ヒドロキシアバ

タイト、ゼオライト、窒化ホウ素、セラミックスパウダーなどの無機粉末、ナイロンパウダー、ポリエチレンパウダー、ポリスチレンパウダー、ベンゾグアナミンパウダー、ポリ四弗化エチレンパウダー、ジスチレンベンゼンポリマーパウダー、エボキシパウダー、アクリルパウダー、微結晶性セルロースなどの有機粉末、酸化チタン、酸化亜鉛などの無機白色顔料、酸化鉄（ベンガラ）、チタン酸鉄などの無機赤色系顔料、γ酸化鉄などの無機褐色系顔料、黄酸化鉄、黄土などの無機黄色系顔料、黒酸化鉄、カーボンブラックなどの無機黑色系顔料、マンゴバイオレット、コバルトバイオレットなどの無機紫色系顔料、酸化クロム、水酸化クロム、チタン酸コバルトなどの無機緑色系顔料、群青、紺青などの無機青色系顔料、酸化チタン被膜雲母、酸化チタン被膜オキシ塩化ビスマス、オキシ塩化ビスマス、酸化チタン被膜タルク、魚鱗箔、着色酸化チタン被膜雲母などのパール顔料、アルミニウムパウダー、カッパーパウダーなどの金属粉末顔料、赤色201号、赤色202号、赤色204号、赤色205号、赤色220号、赤色226号、赤色228号、赤色405号、橙色203号、橙色204号、黄色205号、黄色401号および青色404号などの有機顔料、赤色3号、赤色104号、赤色106号、赤色227号、赤色230号、赤色401号、赤色505号、橙色205号、黄色4号、黄色5号、黄色202号、黄色203号、緑色3号および青色1号のジルコニウム、バリウムまたはアルミニウムレーキなどの有機顔料、クロロフィル、β-カロチンなどの天然色素、スクワラン、流動パラフィン、ワセリン、マイクロクリスタリンワックス、オケゾライト、セレシン、ミリスチン酸、パルミチン酸、ステアリン酸、オレイン酸、イソステアリン酸、セチルアルコール、ヘキサデシルアルコール、オレイルアルコール、2-エチルヘキサン酸セチル、パルミチン酸2-エチルヘキシル、ミリスチン酸2-オクチルドデシル、ジ-2-エチルヘキサン酸ネオペンチルグリコール、トリ-2-エチルヘキサン酸グリセロール、オレイン酸-2-オクチルドデシル、ミリスチン酸イソプロピル、トリイソステアリン酸グリセロール、トリヤシ油脂肪酸グリセロール、オリーブ油、アボガド油、ミツロウ、ミリスチン酸ミリスチル、ミンク油、ラノリンなどの各種炭化水素、シリコーン油、高級脂肪酸、油脂類のエステル類、高級アルコール、ロウなどの油性成分、アセトン、トルエン、酢酸ブチル、酢酸エステルなどの有機溶剤、アルキド樹脂、尿素樹脂などの樹脂、カンファ、クエン酸アセチルトリプチルなどの可塑剤、紫外線吸収剤、酸化防止剤、防腐剤、界面活性剤、保湿剤、香料、水、アルコール、増粘剤などが挙げられる。

【0029】この化粧料の形態は、とくに限定されるものではなく、粉末状、ケーキ状、ペンシル状、スティック状、軟膏状、液状、乳液状、クリーム状などである。

【0030】なお、この発明は次のような実施形態として具現化することも可能である、・ガラスフレークに白金などの貴金属を付着させ、そこにアナース型のチタニアを付着させ、600°C以下に加熱することにより、ルチル型チタニアからなる被膜を備えたガラスフレークを製造する方法。

#### 【0031】

【実施例】以下に実施例および比較例を挙げてこの発明をより詳細に説明するが、この発明の要旨を越えない限り、以下の実施例に限定されるものではない。まず、ガラスフレークに金属酸化物を被膜した真珠光沢顔料について説明する。

#### 【0032】(実施例1)～(実施例4)

Cガラス ( $\text{SiO}_2$ : 65重量%、 $\text{Al}_2\text{O}_3$ : 4重量%、 $\text{CaO}$ : 14重量%、 $\text{MgO}$ : 3重量%、 $\text{B}_2\text{O}_3$ : 5重量%、 $\text{Na}_2\text{O}$ : 8重量%、 $\text{K}_2\text{O}$ : 1重量%) を1, 200°Cで熔融し、円筒形にブローし延伸薄膜化して冷却固化することにより所定の厚さにし、それを粉碎分級して、所定の厚さ、粒度およびアスペクト比を有するガラスフレークを製造した。このガラスフレークを硫酸チタニル溶液中に懸濁させ、この懸濁液を加熱し1時間沸騰させることにより、ガラスフレーク表面に種々の厚さのチタニアを被膜させ、沪過水洗後乾燥させ、その後600°Cで30分間熱処理して、チタニア被膜を備えたガラスフレークを得た。チタニア被膜の結晶系をX線回折で調べたところ、いずれもアナース型であった。

【0033】ここで、チタニア被膜の厚さによりガラスフレークの発色が異なり、またガラスフレークの厚さおよび粒度により比表面積が異なるため、各実施例で目的とするチタニア被膜を得るための条件は一義的には決定できない。そのため、チタニア被膜の形成段階でガラスフレークを懸濁液中から適宜サンプリングし、その色目を確認しながら硫酸チタニルの添加量を加減して、任意の色調のガラスフレークを製造した。

【0034】これら種々の厚さ、粒度およびアスペクト比を有するガラスフレークを、直径6.0mm×高さ1.0mmのシリカのセル中に詰め、それを色彩色差計（ミノルタ社製CR300）で明度（L値）を測定した。また、光沢計（日本電色工業株式会社製 VGS-1001D P）で、45°/0°の拡散反射率を測定し、輝度を評価した。これらガラスフレークの特性および輝度評価の結果を、下記「表4」に示す。

【0035】(比較例1)～(比較例3)市販のアナース型のチタニア被膜を備えたマイカと、ガラスフレーク(RCF-140 日本板硝子社製)に上記実施例の方法でアナース型のチタニア被膜を形成したものについて、上記と同様の方法で、明度（L値）および45°/0°の拡散反射率を測定し、その輝度を評価した。その結果を、下記「表4」に併せて示す。なお、比較例3のガラスフレークには、貴金属は付着していない。

【0036】実施例1～4のガラスフレークは、いずれすことが判る。

も輝度（L値および拡散反射率）が比較例1および2の

マイカに比べ高く、非常に澄んだ明るく高い光輝感を示

【0037】

【表4】

アナタス型のチタニア被膜を備えたガラスフレークおよびマイカの輝度と光沢性

実施例	1	2	3	4	比較例1	2	3
母材	ガラス	ガラス	ガラス	ガラス	マイカ	マイカ	ガラス
平均厚さ(μm)	2.3	2.3	2.3	1.3	0.4	0.6	5.0
平均粒径(μm)	450	80	40	25	40	80	140
アスペクト比	196	35	17	19	100	113	28
反射色	シルバー	シルバー	シルバー	赤	シルバー	シルバー	シルバー
明度(L値)	93	92	91	91	88	89	90
拡散反射率	66	62	61	63	52	54	60

【0038】（実施例5）～（実施例8）

上記実施例1～4と同様にして、所定の形状のガラスフレークを製造した。このガラスフレークを塩化白金酸を添加した四塩化チタン溶液中に懸濁させ、この懸濁液を加熱し1時間沸騰して、ガラスフレーク表面に種々の厚さのチタニア被膜を設けた。このガラスフレークを沪過水洗後乾燥させ、その後600°Cで30分間熱処理した。チタニア被膜の結晶系をX線回折で調べたところ、いずれもルチル型であった。これは、ガラスフレークに付着した白金が、ルチル型への転移を促進する触媒とし

て作用したためと考えられる。これら種々の厚さ、粒度およびアスペクト比を有するガラスフレークについて、上記実施例1～4と同様にして輝度を評価した。その結果を下記「表5」に示す。

【0039】（比較例4）～（比較例7）

市販のルチル型のチタニア被膜を備えるマイカについて、上記同様にして輝度を評価した。その結果を下記「表6」に示す。

【0040】

【表5】

ルチル型のチタニア被膜を備えたガラスフレークの輝度と光沢性

実施例	5	6	7	8
母材	ガラス	ガラス	ガラス	ガラス
平均厚さ(μm)	2.3	1.3	1.3	0.7
平均粒径(μm)	300	80	80	25
アスペクト比	130	62	62	36
反射色	シルバー	ゴールド	赤	青
明度(L値)	95	94	93	92
拡散反射率	70	62	74	74

【0041】

【表6】

ルチル型のチタニア被膜を備えたマイカの輝度と光沢性

比較例	4	5	6	7
母材	マイカ	マイカ	マイカ	マイカ
平均厚さ(μm)	0.4	0.4	0.4	0.6
平均粒径(μm)	40	40	40	80
アスペクト比	100	100	100	133
反射色	シルバー	ゴールド	赤	青
明度(L値)	91	90	90	89
拡散反射率	50	60	65	63

【0042】「表5」および「表6」より、実施例5～8のガラスフレークは、いずれも輝度(L値および拡散反射率)が比較例4～7のマイカに比べ高く、非常に澄んだ明るく高い光輝感を示すことが判る。

【0043】つぎに、上記チタニア被膜を備えたガラス化粧料に関する官能評価

フレークすなわち真珠光沢顔料を配合した化粧料について説明する。化粧料の評価は、下記「表7」に基づきパネラー10人による5段階の官能評価により行った。

【0044】

【表7】

評価\項目	のび	密着感	滑らかさ	光輝感	色のきれいさ
1	悪い	ない	ない	ない	汚い
2	やや悪い	ややない	ややない	あまりない	ややくすむ
3	普通	普通	普通	ややある	普通
4	ややよい	ややある	ややある	ある	きれい
5	よい	非常にある	非常にある	非常に高い	非常にきれい

【0045】官能評価の結果は、パネラー10名の5段階評価の平均値であり、その評価を分かり易くするために下記の記号で表す。

- ◎・・・4.5以上5.0まで
- ・・・3.5以上4.5未満
- ・・・2.5以上3.5未満
- △・・・1.5以上2.5未満

×・・・1.0以上1.5未満

【0046】(実施例9)：パウダーファンデーション下記「表8」に示す材料からなるパウダーファンデーションを製造した。

【0047】

【表8】

(1) 酸化チタン	7
(2) タルク	20
(3) 白雲母	3
(4) 実施例2のガラスフレーク	55
(5) ナイロンパウダー	2
(6) 赤色酸化鉄	0.5
(7) 黄色酸化鉄	1
(8) 黒色酸化鉄	0.1
(9) シリコーンオイル	1
(10) バルミチン酸2-エチルヘキシル	9
(11) セスキオレイン酸ソルビタン	1
(12) 防腐剤	0.3
(13) 香料	0.1 (重量%)

【0048】上記材料(1)～(8)をヘンシェルミキサーで混合し、この混合物に上記材料(9)～(13)を加熱溶解させ混合したものを添加混合し、これをパライザーで粉碎した。さらに、これを直径5.3mmの中皿に吐出し、160kg/cm<sup>2</sup>の圧力で押圧成形し、パウダーファンデーションを製造した。この化粧料の官能評価の結果を、下記「表9」に示す。

【0049】(比較例8)：パウダーファンデーション上記材料(4)ガラスフレークを比較例1のマイカに置換し、それ以外を実施例9と同様にしてパウダーファン

デーションを製造した。この化粧料の官能評価の結果を、下記「表9」に示す。

【0050】(比較例9)：パウダーファンデーション上記材料(4)ガラスフレークを比較例3のガラスフレークに置換し、それ以外を実施例9と同様にしてパウダーファンデーションを製造した。この化粧料の官能評価の結果を、下記「表9」に併せて示す。

【0051】

【表9】

項目	のび	密着感	滑らかさ	光輝感	色のきれいさ
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実施例9	○	○	○	◎	◎
比較例8	○	○	○	○	○
比較例9	●	●	△	○	◎

【0052】「表9」より、実施例9の化粧料は、比較例8と比べ光輝感および色のきれいさで、比較例9と比べのび、密着感および滑らかさで優れていることが判る。

【0053】(実施例10) : ブラッシャー下記「表10」に示す材料からなるブラッシャーを製造した。

【0054】

【表10】

(1) タルク	12.6
(2) 絹雲母	8.1
(3) マイカ	25.4
(4) 実施例3のガラスフレーク	45.0
(5) 赤色226号	0.4
(6) スクワラン	3.0
(7) パルミチン酸2-エチルヘキシル	5.0
(8) 防腐剤	0.3
(9) 香料	0.2 (重量%)

【0055】上記材料(1)～(5)をヘンシェルミキサーで混合し、この混合物に上記材料(6)～(9)を加熱溶解させ混合したものを作り、バーベライザーを用いてこれを粉碎した。さらに、これを4×6cmの中皿に吐出し、120kg/cm<sup>2</sup>で押圧成形して、ブラッシャーを製造した。この化粧料の官能評価の結果を、下記「表11」に示す。

【0056】(比較例10) : ブラッシャー  
実施例10の材料(4)ガラスフレークを比較例2のマイカに置換し、それ以外を実施例10と同様にしてブ

ッシャーを製造した。この化粧料の官能評価の結果を、下記「表11」に示す。

【0057】(比較例11) : ブラッシャー  
実施例10の材料(4)ガラスフレークを比較例3のガラスフレークに置換し、それ以外を実施例10と同様にしてブラッシャーを製造した。この化粧料の官能評価の結果を、下記「表11」に併せて示す。

【0058】

【表11】

項目	のび	密着感	滑らかさ	光輝感	色のきれいさ
実施例10	○	○	○	◎	◎
比較例10	○	○	○	○	○
比較例11	●	●	△	○	◎

【0059】「表11」より、実施例10の化粧料は、比較例10と比べ光輝感および色のきれいさで、比較例11と比べのび、密着感、滑らかさおよび光輝感で優れていることが判る。

【0060】(実施例11) : ネイルエナメル

下記「表12」に示す材料からなるネイルエナメルを製造した。

【0061】

【表12】

(1) ニトロセルロース	12
(2) 変成アルキド樹脂	12
(3) クエン酸アセチルトリプチル	5
(4) 酢酸n-ブチル	36.4
(5) 酢酸エチル	6
(6) n-ブチルアルコール	2
(7) トルエン	21

(8) 酸化鉄顔料	0.5
(9) 二酸化チタン	0.1
(10) 実施例7のガラスフレーク	3
(11) マイカ	1
(12) 有機変成モンモリロナイト	1 (重量%)

【0062】上記材料(1)～(7)(ただし材料(4)は一部分)を溶解し、この溶液に材料(12)と材料(4)の残部とを混合してゲル状にしたもの添加混合し、さらに材料(8)～(11)を添加混合した。この混合物を所定の容器に充填し、ネイルエナメルを製造した。この化粧料の官能評価の結果を、下記「表13」に示す。

【0063】(比較例12)：ネイルエナメル  
実施例11の材料(10)ガラスフレークを比較例6のマイカに置換し、それ以外は実施例11と同様にしてネ

イルエナメルを製造した。この化粧料の官能評価の結果を、下記「表13」に示す。

【0064】(比較例13)：ネイルエナメル  
実施例11の材料(10)ガラスフレークを比較例3のガラスフレークに置換し、それ以外は実施例11と同様にしてネイルエナメルを製造した。この化粧料の官能評価の結果を、下記「表13」に示す。

【0065】

【表13】

項目	のび	密着感	滑らかさ	光輝感	色のきれいさ
実施例11	○	○	◎	◎	◎
比較例12	○	○	○	○	○
比較例13	●	●	△	○	◎

【0066】「表13」より、実施例11の化粧料は、比較例12と比べ滑らかさ、光輝感および色のきれいさで、比較例13と比べのび、密着感、滑らかさおよび光輝感で優れていることが判る。

【0067】(実施例12)：乳化ファンデーション

下記「表14」に示す材料からなる乳化ファンデーションを製造した。

【0068】

【表14】

(1) ステアリン酸	0.4
(2) イソステアリン酸	0.3
(3) 2-エチルヘキサン酸セチル	4
(4) 流動パラフィン	1.1
(5) ポリオキシエチレン(10)ステアリルエーテル	2
(6) タルク	8
(7) 顔料	4
(8) セチルアルコール	0.3
(9) 防腐剤	0.07
(10) 実施例6のガラスフレーク	1.0
(11) トリエタノールアミン	0.42
(12) プロピレングリコール	5
(13) 防腐剤	0.02
(14) イオン交換水	54.19
(15) 香料	0.3 (重量%)

【0069】上記材料(1)～(9)を85℃で溶解させ混合し、これに上記材料(10)を添加し均一に分散させた。また、これに上記材料(11)～(14)を85℃で溶解させ混合した混合物を徐々に添加し乳化させた。乳化時の温度を10分間保持して攪拌した後、攪拌

しながら45℃まで冷却した。これに材料(15)を加え35℃まで攪拌冷却を続け、その後これを容器に充填して乳化ファンデーションを得た。この化粧料の官能評価の結果を、下記「表15」に示す。

【0070】(比較例14)：乳化ファンデーション

実施例12の材料(10)ガラスフレークを比較例5のマイカに置換し、それ以外を実施例12と同様にして乳化ファンデーションを製造した。この化粧料の官能評価の結果を、下記「表15」に示す。

【0071】(比較例15)：乳化ファンデーション

実施例12の材料(10)ガラスフレークを比較例3の

ガラスフレークに置換し、それ以外を実施例12と同様にして乳化ファンデーションを製造した。この化粧料の官能評価の結果を、下記「表15」に併せて示す。

【0072】

【表15】

項目	のび	密着感	滑らかさ	光輝感	色のきれいさ
実施例12	○	○	◎	◎	◎
比較例14	○	○	○	○	△
比較例15	●	●	△	○	◎

【0073】「表15」より、実施例12の化粧料は、比較例14と比べ滑らかさ、光輝感および色のきれいさで、比較例15と比べのび、密着感、滑らかさおよび輝感で優れていることが判る。

【0074】(実施例13)：口紅

下記「表16」に示す材料からなる口紅を製造した。

【0075】

【表16】

(1) 炭化水素ワックス	20
(2) キャンデリラワックス	3
(3) グリセリルイソステアレート	40
(4) 流動パラフィン	26.8
(5) 二酸化チタン	4
(6) 実施例7のガラスフレーク	4
(7) 有機顔料	2
(8) 香料	0.2 (重量%)

【0076】上記材料(1)～(4)を85℃で加熱溶解させ、これに(5)～(7)を加え攪拌混合した後、さらに(8)を混合攪拌し、その後所定の容器に充填して口紅を得た。この化粧料の官能評価の結果を、下記「表17」に示す。

17」に示す。

【0078】(比較例17)：口紅

実施例13の材料(6)ガラスフレークを比較例3のガラスフレークに置換し、それ以外を実施例13と同様にして口紅を製造した。この化粧料の官能評価の結果を、下記「表17」に併せて示す。

【0079】

【表17】

【0077】(比較例16)：口紅  
実施例13の材料(6)ガラスフレークを比較例6のマイカに置換し、それ以外を実施例13と同様にして口紅を製造した。この化粧料の官能評価の結果を、下記「表

項目	のび	密着感	滑らかさ	光輝感	色のきれいさ
実施例13	○	○	◎	◎	◎
比較例16	○	○	○	○	○
比較例17	●	●	△	○	◎

【0080】「表17」より、実施例13の化粧料は、比較例16と比べ滑らかさ、光輝感および色のきれいさ、比較例17と比べのび、密着感、滑らかさおよび光輝感で優れていることが判る。

下記「表18」に示す材料からなるアイシャドーを製造した。

【0082】

【表18】

【0081】(実施例14)：アイシャドー

(2) 白雲母	20
(3) 実施例8のガラスフレーク	40
(4) 顔料	12
(5) スクワラン	4
(6) セチル2-エチルヘキサンオエート	1.9
(7) ソルビタンセスキオレート	0.8
(8) 防腐剤	0.1
(9) 香料	0.2 (重量%)

【0083】上記材料(1)～(4)をヘンシェルミキサーで混合し、これに(5)～(9)を加熱混合したものを吹き付け混合した後粉碎した。これを所定の中皿に吐出して、アイシャドーを得た。この化粧料の官能評価の結果を、下記「表19」に示す。

【0084】(比較例18)：アイシャドー  
実施例14の材料(3)ガラスフレークを比較例7のマイカに置換し、それ以外を実施例14と同様にしてアイシャドーを製造した。この化粧料の官能評価の結果を、

下記「表19」に示す。

【0085】(比較例19)：アイシャドー  
実施例14の材料(3)ガラスフレークを比較例3のガラスフレークに置換し、それ以外を実施例14と同様にしてアイシャドーを製造した。この化粧料の官能評価の結果を、下記「表19」に示す。

【0086】

【表19】

項目	のび	密着感	滑らかさ	光輝感	色のきれいさ
実施例14	◎	◎	◎	◎	◎
比較例18	○	○	○	○	△
比較例19	●	●	△	○	◎

【0087】「表19」より、実施例14の化粧料は、比較例18と比べのび、密着感、滑らかさ、光輝感および色のきれいさで、比較例19と比べのび、密着感、滑らかさおよび光輝感で優れていることが判る。

【0088】

【発明の効果】この発明は、以上のように構成されているため、次のような効果を奏する。請求項1に記載の発明の真珠光沢顔料によれば、平均厚さ0.1～2.5μm、平均粒径1～300μmおよびアスペクト比10～50であり、母材がシリカを45～75重量%含有する表面が平滑なガラスフレークであって、さらに母材表面が酸化チタンなどの金属酸化物で被膜された真珠光沢顔料であるので、化粧料材料としてくすみがなく、非常に

良好な光輝感を発現し、肌上のざらつき感がなく、のび、フィット感に優れる安価な真珠光沢顔料を提供することができる。

【0089】請求項2に記載の発明の真珠光沢顔料によれば、請求項1の発明の効果に加えて、母材の表面に貴金属およびチタニアが付着するので、600℃以下の加熱で緻密で安定型のルチル型チタニアの膜が形成される。

【0090】請求項3に記載の発明の化粧料によれば、この真珠光沢顔料を化粧料材料として用いるので、肌上でののびがよくかつフィット感に優れ、ざらつき感を生じさせることのない、光輝感に優れる発色のきれいな化粧料を提供することができる。

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[Title of Invention] Pearlescent pigment and the cosmetic in which it is blended

[Abstract]

[Problem] To provide an inexpensive pearlescent pigment that, when blended into cosmetic, has no lackluster, exhibits very good brightness, gives no feeling of roughness on the skin and has excellent spreading and gives good feel of fit and, further, to provide the cosmetic that contains it and gives excellent feel of brightness.

[Means of Solution] Glass flake containing silica ( $\text{SiO}_2$ ) by 45 ~ 75 wt % and having an average thickness of 0.1 ~ 2.5  $\mu\text{m}$ , average particle size of 1 ~ 300  $\mu\text{m}$  and an aspect ratio of 10 ~ 500 is made by the melting method. The aspect ratio means the value obtained by dividing the average particle size with the average thickness (average particle size/average thickness).

[Claims of the Patent]

[Claim 1] Pearlescent pigment whose parent material contains silica ( $\text{SiO}_2$ ) by 45 ~ 75 wt %, the pigment having an average thickness of 0.1 ~ 2.5  $\mu\text{m}$ , average particle size of 1 ~ 300  $\mu\text{m}$  and an aspect ratio of 10 ~ 500.

[Claim 2] The pearlescent pigment described in Claim 1 in which, on the surface of the said parent material, precious metal and titania are attached.

(1)

[Claim 3] Cosmetic in which the pearlescent pigment described in Claim 1 or 2 is blended.

[Detailed Description of the Invention]

[0001]

[Field of Technology Where the Invention Belongs] This invention is related to the pearlescent pigment for which the composition of parent material, the thickness, particle size and aspect ratio are within fixed ranges and to the cosmetic in which this pigment is blended. Further, the invention is related also to the said pearlescent pigment which is the glass flake having the coated film of metal oxide.

[0002]

[Existing Technology] As the bright, flaky powder that exhibits pearlescence, the so called pearl mica obtained by using the natural or synthetic mica as the base material and coating its surface with titanium oxide or iron oxide has been known from the past. However, as the mica has cleaving characteristics, difference of level can form easily on its surface and so, frequently, its surface smoothness is inadequate. For this reason, it can not be said that the pearlescent pigment from the base material of mica exhibits good brightness. Also, as many impurities are contained in the natural mica, the pearlescent pigment using it as the base material causes lackluster when blended in cosmetic.

[0003] As a pearlescent pigment, Kokai JP No. 176515 – 1997 describes a flaky powder coated with metal oxide having an average shape ratio (average thickness/ average particle size) of 1/9 ~ 1 and particle size of 25 ~ 500  $\mu\text{m}$ . When this flaky powder is used in a cosmetic material, the calculated thickness becomes more than 2.78  $\mu\text{m}$  and so it gives rough feeling on the skin; also, as the average shape ratio is large and the shape is close to that of a cube, spreading on the skin or the feel of fit is poor; further, compared to the thin flake of equal weight, number of sheets is smaller and so there is the problem of less feel of brightness due to reflection.

[0004] Also, Kokai JP No. 116507 – 1994 describes a pearlescent pigment that uses, as the base material, the flaky silica glass made from metal alkoxide and is coated with titania or zirconia. This flaky silica glass has the cost problem because the metal alkoxide is very expensive. Also, as the silica glass has higher silica content high and higher hardness in comparison to the common glass, it is pulverized when mixed during the material blending process in the case of using it as the cosmetic material and so there is the danger that its particle size can not be maintained. When the particle size becomes smaller, there is the advantage of the uniform dispersion in the cosmetic material becoming easier but, on the other hand, there is the problem that it is difficult to express the brightness as the pearlescent pigment.

[0005] Further, Kokai JP No. 187770 – 1987 describes a UV ray- blocking pigment made by coating the glass flake with fine grain particles of titanium oxide. However, this UV

ray-blocking pigment is coated with an amount of titanium oxide by which the pearlescence is actually not expressed.

[0006]

[The Problem That the Invention Intends to Solve] As has been described above, the blending of pearlescent pigment in the cosmetic products has been practiced widely from the past but the pearlescent pigment that uses the natural or synthetic mica as its base material has the problem that, because of its inadequate surface smoothness, it can not be said to express good brightness. Also, in the case of using the natural mica as the base material, impurities are contained and so, when blended in cosmetic, this causes the lack-luster. Further, in the case of using the flaky silica glass as the base material, there are problems of the cost and the difficulty of maintaining the particle size.

[0007] This invention was accomplished in view of such problems of the existing technology. Its objective is to provide an inexpensive pearlescent pigment that, when blended into cosmetic, has no lackluster, exhibits very good brightness, gives no feeling of roughness on the skin and has excellent spreading and gives good feel of fit. Further, the objective is to provide the cosmetic that has good spreading and feel of fit, does not generate rough feel and has excellent brightness.

[0008]

[The Means for Solving the Problem] To achieve the above mentioned objective, the parlescent pigment of the invention described in Claim 1 is the one whose parent material contains silica ( $\text{SiO}_2$ ) by 45 ~ 75 wt %, the pigment having an average thickness of 0.1 ~ 2.5  $\mu\text{m}$ , average particle size of 1 ~ 300  $\mu\text{m}$  and an aspect ratio of 10 ~ 500. Here, the aspect ratio means the value obtained by dividing the average particle size with the average thickness (average particle size/ average thickness).

[0009] The pearlescent pigment of the invention described in Claim 2 is the one described in Claim 1 in which, on the surface of the said parent material, precious metal and titania are attached.

[0010] The cosmetic material of the invention described in Claim 3 is the one in which the pearlescent pigment described in Claim 1 or 2 is blended.

[0011]

[Mode of Application of the Invention] In the following, detailed explanation is given on the mode of application of this invention. The pearlescent pigment of this invention is the one in which the base material contains silica ( $\text{SiO}_2$ ) by 45 ~ 75 wt %. As for this base material, the example is the glass flake that is made by the melting method. The glass flake can be made by the known technologies, e.g. the methods described in, for example, JP No. 17148 – 1966, JP No. 3541 – 1970. Thus, the molten glass is extruded from a circular slit and air is injected inside the glass to expand this into a hollow cylinder to make the thin and uniform glass film and this is pulverized to make the glass flake. This

glass flake is made by melting inexpensive raw material and so its cost can be kept low. Also, as the molten glass having free surface is cooled and solidified, its surface is very smooth. Also, as the material is amorphous and does not have the cleaving characteristics, difference of level is not formed on its surface. Also, compared with the silica glass which contains silica by more than 80 wt %, it has some flexibility and, so, when blended in the cosmetic, pulverization does not occur easily and the particle size at the time of blending can be maintained. As for the glass, that of any composition is good as long as melt-shaping is possible and the examples are soda lime glass, C glass, E glass, etc. which are commonly used. These glasses contain the silica by the above said range.

[0012] Also, by pulverizing and classifying the glass film of average thickness of 1 ~ 2.5  $\mu\text{m}$ , the glass flake of average particle size 1 ~ 300  $\mu\text{m}$  and aspect ratio of 10 ~ 500 is made. Because of the production technology, the glass flake can not be made thinner than 0.1  $\mu\text{m}$ . On the other hand, when it is thicker than 2.5  $\mu\text{m}$ , this generates the feel of roughness in the cosmetic in which it was blended and it also reduces the brightness. When the aspect ratio is smaller than 10, the spreading and the feel of fit of the cosmetic in which it was blended is made worse; on the other hand, when it is greater than 500, spreading of the cosmetic onto the skin is made poor and the feel of roughness is made excessively strong. When the average particle size is less than 1  $\mu\text{m}$ , sufficient brightness can not be imparted to the cosmetic in which it was blended; on the other hand, if it is greater than 300  $\mu\text{m}$ , the particles show too much in the cosmetic in which it is blended and the finishing becomes unnatural.

[0013] When the shape of the base material is within the above said range, property of the glass flake varies with the silica content of the base material. When the silica content is higher than 75 wt %, the production by the melting method is difficult and the production by the sol-gel method actually becomes the main stream. The glass that has high silica content and is made by the sol-gel method is called [silica glass], hereinafter. Flake of the silica glass whose shape is in the above said range has high hardness and is brittle as mentioned above and so, when an external force above a certain level is applied, it breaks easily. For example, when ultra sonic wave is irradiated to the flake of silica glass, its average particle size is found to decrease. Specifically, when the laser diffraction particle size distribution measuring apparatus (Pro 7000 S made by Seishin Kogyo Col) attached with the ultra sonic wave irradiating apparatus is used to obtain 65 W output for 1 minute and the ultrasonic wave is irradiated to the flake to silica glass, its average particle size changed as shown in the [Table 1] below.

[0014] [Table 1]

Change in particle size when ultra sonic wave is irradiated on the flake of silica glass

Item	Initial average particle size ( $\mu\text{m}$ )	After the irradiation of ultrasonic wave ( $\mu\text{m}$ )
Sample 1	6.02	5.90
Sample 2	9.36	9.20
Sample 3	15.62	15.40

Sample 4	24.49	21.79
Sample 5	25.93	23.30
Sample 6	26.69	25.13
Sample 7	28.41	23.10
Sample 8	50.19	35.58
Sample 9	55.50	38.48
Sample 10	58.93	39.04

**Table 1. Footnote.** For the samples 1 ~ 10, SG series (made by Nippon Sheet Glass K. K.) were used.

[0015] Also, it was confirmed that, as the irradiation time of ultrasonic wave increased, average particle size of the flake of silica glass decreased. Specifically, when the ultra sonic cleansing apparatus (made by Velvo Clear Commerce Co , VS - 70R) was used to obtain 60 W output and the ultrasonic wave was irradiated to the flake of silica glass, its average particle size changed as shown in [Table 2]

[0016] [Table 2]

Change of particle size with time when ultrasonic wave was irradiated to the flake of silica glass

Item/ irradiation time	0 min	0.5 min	1 min	2 min	5 min
Sample 1 ( $\mu\text{m}$ )	23.19	14.70	13.63	12.35	11.25
Sample 2 ( $\mu\text{m}$ )	69.08	37.79	34.30	30.74	27.89
Sample 3 ( $\mu\text{m}$ )	183.80	85.73	67.70	60.04	58.05

Note) For the samples 1 ~ 3, SG series (made by Nippon Sheet Glass K. K.) were used.

[0017] From [Table 1] and [Table 2], it is seen that when the particle size of silica glass is greater, it breaks more easily by ultra sonic wave. With respect to the time elapsed, it is seen that the breaking occurs easily during the initial period of the ultra sonic wave irradiation. In this way, the flake of silica glass breaks by the impact of ultrasonic wave but this phenomenon is not observable with the glass flake. This is believed to be due to the fact that glass flake is not so hard as silica glass and that it has some flexibility. Consequently, with pearlescent pigment that uses the glass flake as the base material, the initial particle size can be maintained better than the flake of silica glass when blended and mixed into other materials as the material of cosmetic and, as the result, the brightness can be expressed more effectively in the cosmetic material also. As to the silica content of the glass flake, 50 ~ 70 wt %, preferably 55 ~ 65 wt %, is good to let the base material have the necessary strength and proper flexibility.

[0018] As the name indicates, this pearlescent pigment shows the luster like that of pearl in appearance and this can be obtained by installing on the glass flake the coating film consisting of metal oxide such as titania ( $\text{TiO}_2$ ), zirconia or iron oxide. As for the method of forming this coating film, one can use the known technology which is described in, for

example, JP No. 25644 – 1968, Kokai JP No. 34529 – 1972. Specifically, the glass flake is suspended in the titanyl sulfate solution or titanium tetra chloride solution and, by raising the temperature of this solution, the titania is precipitated and the coating film is installed on the glass flake. However, the method is not limited to this and one can use any method as long as it can install a thin coating film on the glass flake.

[0019] By controlling the thickness of the coating film on the glass flake, an optional color tone due to the interference can be expressed. As for the thickness of this coating film, 20 ~ 25 nm is preferred. When it is less than 20 nm, brightness can not be expressed and, on the other hand, when it is thicker than 250 nm, greater amount of raw material is needed and so this is not preferable for the cost.

[0020] When titania is used for this coating film, the glass flake is heat-treated at 800 ~ 1200 deg C after the formation of coating film in many cases. This heat treatment is conducted to convert the anatase type to the rutile type as there are 3 crystal systems, i.e. the anatase type, bluekite (phonetic translation) type and rutile type, in titania. When the titania coating film is installed by the precipitation from the solution described above, first the anatase type precipitates out. Anatase type is chemically unstable compared to the rutile type and, therefore, when durability and weatherability are required of the glass flake, the rutile type is preferred over the anatase type. The titania coating film of rutile type forms more dense film than the anatase type and so it expresses higher brightness, i.e. more vivid color. Therefore, as the coating film of glass flake, that which consists of the titania of rutile type is preferred and so the process is directed it.

[0021] When the heat treatment temperature for the above mentioned conversion of crystal system is below 800 deg C, crystal system of titania remains as the anatase type; but, on the other hand, when it is higher than 800 deg C, conversion to the rutile type is known to occur. However, when heating is done to over 800 deg C, there are cases in which the glass flake deforms. To prevent this deformation, the present inventors conducted extensive studies and, as the result, found out a method of converting to the rutile type even at a heating temperature below 800 deg C. It is the method in which, at the time of precipitating titania from the said solution, a minute amount of precious metal is attached to the glass flake as a catalyst. Here, the precious metal indicates gold, silver and platinum family (Ru, Rh, Pd, Os, Ir, Pt). As to the method of attaching precious metal to the glass flake, there is no particular restriction. An example is the method in which the glass flake is put into the solution of chloro planitinic acid and kept there for a while. In this method, it was confirmed that the conversion of crystal system to the rutile type occurs by the heat treatment below 600 deg C.

[0022] Depending on the refractive index of the coating film on the glass flake, the thickness of coating film which expresses a certain color tone varies somewhat but, in general, the relation between the thickness of coating film and the coloring (reflected light) is as shown in [Table 3] below.

[0023] [Table 3]

Coloring	Thickness of coating film (nm)
Silver	40 ~ 60
Yellow	60 ~ 80
Red	80 ~ 100
Blue	100 ~ 140
Green	120 ~ 160

[0024] By blending the glass flake of specific shape having the coating film of the above said metal oxide, i.e. the pearlescent pigment, one can obtain the cosmetic material that exhibits clear coloring without lackluster, has no feel of roughness on the skin and, further, has excellent spreading and feel of fit on the skin.

[0025] As for the blending ratio of the pearlescent pigment in this cosmetic, 1 ~ 100 wt % is preferred. When the blending ratio is less than 1 wt %, the brightness of pearlescent pigment is not expressed sufficiently. On the other hand, even if it is 100 wt %, it can combine with the human fat that is present on the skin and can function as the cosmetic material.

[0026] In this cosmetic material, a wide range of cosmetic material such as the facial cosmetic, makeup cosmetic, hair cosmetic are included. Among these, this pearlescent pigment is used suitably particularly in the makeup cosmetic such as the foundation, white powder, eye shadow, brusher, make up base, nail enamel, eye liner, mascara, rouge, fancy powder, etc.

[0027] Depending on the purpose of the cosmetic material, this pearlescent pigment can be given a treatment for making it suitably hydrophobic. As for the method of hydrophobic treatment, examples are: first, the method of treatment by using the silicone compound such as methyl hydrogen poly siloxane, high viscosity silicone oil and silicon resin, etc., secondly, the method of treatment by using the surfactant such as anionic surfactant, cationic surfactant, etc., thirdly, the method of treatment by using the polymeric compound such as nylon, poly methyl methacrylate, poly ethylene, Teflon, poly amino acid, fourthly, the method of treatment by using the compound containing perfluoro group, lecithin, collagen, metal soap, oleophilic wax, poly hydric alcohol partial ester or complete ester, fifthly, the method of treatment that combines these. However, the method is not restricted to the above mentioned methods if a method is applicable to the common hydrophobic treatment of powder.

[0028] In this cosmetic material, when necessary, one can blend suitably other materials that are used commonly in the cosmetics. The examples are: Inorganic powder such as talcum, kaolin, sericite, white mica, gold mica, red mica, black mica, Lithia mica, barmiculite (phonetic translation), magnesium carbonate, calcium carbonate, diatom earth, magnesium silicate, calcium silicate, aluminum silicate, barium silicate, barium sulfate,

strontium silicate, tungstic acid metal salt, silica, hydroxy apatite (phonetic translation), boron nitride, ceramics powder; Organic powder such as nylon powder, poly ethylene powder, benzo guanamine powder, poly tetra fluoro ethylene powder, distyrene benzene polymer powder, epoxy powder, acryl powder, micro crystalline cellulose; Inorganic red-colored pigment such as iron oxide (Bengala), iron titanate; In organic brown colored pigment such as  $\gamma$  iron oxide; Inorganic yellow colored pigment such as iron yellow oxide, ocher; Inorganic black colored pigment such as black iron oxide, carbon black; Inorganic violet colored pigment such as mango violet, cobalt violet; Inorganic green colored pigment such as chromium oxide, chromium hydroxide, cobalt titanate; Inorganic blue colored pigment such as ultra marine blue, Prussian blue; Pearl pigment such as titanium oxide – coated mica, titanium oxide coated oxy chloro bismuth, titanium oxide coated talcum, fish scale foil, colored titanium oxide- coated mica; Metallic powder pigment such as aluminum powder, copper powder; Organic pigment such as Red Color No. 201, Red Color No. 202, Red Color No. 204, Red Color No. 205, Red Color No. 220, Red Color No. 226, Red Color No. 228, Red Color No. 405, Orange Color No. 203, Orange Color No. 204, Yellow Color No. 205, Yellow Color No. 401 and Blue Color No. 404; Organic pigment such as zirconium, barium or aluminum lake of Red Color No. 3, Red Color No. 104, Red Color No. 106, Red Color No. 227, Red Color No. 230, Red Color No. 401, Red Color No. 505, Orange Color No. 205, Yellow color No. 4, Yellow Color No. 5, Yellow Color No. 202, Yellow Color No. 203, Green Color No. 3 Blue Color No. 1; Natural coloring matter such as chlorophyll,  $\beta$ - carotene; Various hydrocarbons such as sqallane, fluid paraffin, Vaseline, micro crystalline wax, ochezolite, ceresin, myristic acid, palmitic acid, stearic acid, oleic acid, iso stearic acid, cetyl alchol, hexa decyl alcohol, oleyl alcohol, cetyl 2- ethyl hexanoate, 2- e thyl hexyl palmitate, 2- octyl dodecyl myristate, neo pentyl glycol di- 2- ethyl hexanoate, glycerol tri –2- ethyl hexanoate, 2- octyl dodecyl oleate, iso propyl myristate, glycerol tri iso stearate, tri cocoanut oil fatty acid glycerol, olive oil, avogard oil, beeswax, myristyl myristate, mink oil, lanolin; Silicone oil, esters of higher fatty acid, oil and fat; Oily component such as higher alcohol, wax, etc.; Organic solvent such as acetone, toluene, butyl acetate, acetic acid ester, etc.; Resin such as alkyd resin, urea resin, etc.; Plasticizing agent such as campha, acetyl tri butyl citrate, etc.; UV ray absorbing agent, antioxidant, preservative, surfactant, moisture retaining agent, perfume, water, alcohol, viscosity increasing agent, etc.

[0029] As to the form of this cosmetic, there is no particular restriction and it can be in the form of powder, cake, pencil, stick, ointment, liquid, latex, cream, etc.

[0030] Further, this invention can be realized by the following mode of application: the method in which a precious metal such as platinum is attached to glass flake and then the titania of anatase type is attached to it and, by heating at below 600 deg C, the glass flake having the coating film that consists of the rutile type titania is made.

[0031]

[Examples of Application] In the following, examples of application and comparative

examples are given to explain this invention in further detail. However, the invention is not limited to these examples of application as long as the key point of this invention is not exceeded. First, explanation is given on the pearlescent pigment prepared by film-coating the glass flake with metal oxide.

[0032] (Example of Application 1) ~ (Example of Application 4)

The C glass ( $\text{SiO}_2$ : 65 wt %,  $\text{Al}_2\text{O}_3$ : 4 wt %,  $\text{CaO}$ : 14 wt %,  $\text{MgO}$ : 3 wt %,  $\text{B}_2\text{O}_3$ : 5 wt %,  $\text{Na}_2\text{O}$ : 8 wt %,  $\text{K}_2\text{O}$ : 1 wt %) was melted at 1,200 deg C and this was blown into the cylindrical shape to stretch it to thin film and this was cooled and solidified to the prescribed thickness. This was pulverized and classified to make the glass flake having the prescribed thickness, particle size and aspect ratio. This glass flake was suspended in the titanyl sulfate solution and the suspension was heated and boiled for 1 hour to film-coat the surface of glass flake with titania to various thickness. After filtration, water-washing and drying, heat treatment was done at 600 deg C for 30 minutes to obtain the glass flake that has the coated film of titania. The crystal system of the titania coating film was examined by X ray diffraction. In all cases it was the anatase type.

[0033] Here, depending on the thickness of titania coating film, coloring of the glass flake varies and, also depending on the thickness and particle size of glass flake, the specific surface area varies. Therefore, the condition for obtaining the desired titania coating film in each example of application can not be determined univocally. At the stage of forming the titania coating film, glass flake was sampled in a suitable way from the suspension and the amount of addition of titanyl sulfate was adjusted while checking the color to make the glass flake of an optional color tone.

[0034] The glass flake having these various thickness, particle size and aspect ratio was packed in a cell of silica of diameter 60 mm x height 10 mm and its lightness (L value) was measured by using the color difference meter (CR300 made by Minolta Co.). Also, by using a gloss meter (VGS- 1001DP made by Nippon Denshoku Kogyo K. K.), the diffuse reflectance of 45°/ 0° was measured and the brightness was evaluated. The properties and results of brightness evaluation of these glass flakes are shown in [Table 4] below.

[0035] (Comparative Example 1) ~ (Comparative Example 3) For the mica that had the coating film of commercially available titania of the anatase type and for the glass flake (RCF- 140 made by Nippon Sheet Glass Co.) on which the titania coating film of anatase type was formed by the method of them example of application described above, the lightness (L value) and the diffuse reflectance of 45°/ 0° were measured by the same method as described above and its brightness was evaluated. The results are shown also in [Table 4] below. Now, in the glass flake of Comparative Example 3, precious metal is not attached.

[0036] It is seen that all of the glass flake of Examples of Application 1 ~ 4 have the brightness (L value and diffuse reflectance)) that is higher in comparison to the mica of

Comparative Examples 1 and 2 are very clear and bright and gives a high feel of brightness.

[0037] [Table 4]

Brightness and glossiness of glass flake and mica having the coating film of titania of the anatase type

Example of Application	1	2	3	4	Comparative Example 1		
					2	3	
Base material	glass	glass	glass	glass	mica	mica	glass
Average thickness ( $\mu\text{m}$ )	2.3	2.3	2.3	1.3	0.4	0.6	5.0
Average particle size ( $\mu\text{m}$ )	450	80	40	25	40	80	140
Aspect ratio	196	35	17	19	100	113	28
Reflected color	silver	silver	silver	red	silver	silver	silver
Lightness (L value)	93	92	91	91	88	89	90
Diffuse reflectance	66	62	61	63	52	54	60

[0038] (Example of Application 5) ~ (Example of Application 8)

By the same procedure as in Examples of Application 1 ~ 4 described above, glass flake of prescribed shape was made. This glass flake was suspended in the titanium tetra chloride solution to which chloro platinic acid was added. This suspension was heated and boiled for 1 hour to install the titania coating film of various thickness on the surface of glass flake. This glass flake was filtered, water-washed and dried and then it was heat treated at 600 deg C for 30 minutes. Crystal system of the titania coating film was examined by X ray diffraction and all were of the rutile type. This is believed to be due to the fact that the platinum that was attached to the glass flake acted as the catalyst which accelerates the conversion to the rutile type. For these glass flake having various thickness, particle size and aspect ratio, the brightness was evaluated by the same procedure as in Examples of Application 1 ~ 4 described above. The results are shown in [Table 5] below.

[0039] (Comparative Example 4) ~ (Comparative Example 7)

For the mica that has the titania coating film of the rutile type that is available commercially, the brightness was evaluated by the same procedure described above. The results are shown in [Table 6] below.

[0040] [Table 5]

Brightness and glossiness of then glass flake having the titanium coating film of rutile type

Example of Application	5	6	7	8
Base material	glass	glass	glass	glass
Average thickness ( $\mu\text{m}$ )	2.3	1.3	1.3	0.7

Average particle size ( $\mu\text{m}$ )	300	80	80	25
Aspect ratio	130	62	62	36
Reflected color	silver	gold	red	blue
Lightness (L value)	95	94	93	92
Diffuse reflectance	70	62	74	74

[0041] [Table 6]

Brightness and glossiness of then mica having the titanium coating film of rutile type

Comparative Example	4	5	6	7
Base material	mica	mica	mica	mica
Average thickness ( $\mu\text{m}$ )	0.4	0.4	0.4	0.6
Average particle size ( $\mu\text{m}$ )	40	40	40	80
Aspect ratio	100	100	100	133
Reflected color	silver	gold	red	blue
Lightness (L value)	91	90	90	89
Diffuse reflectance	50	60	65	63

[0042] From [Table 5] and [Table 6], it is seen that all of the glass flake of Examples of Application 5 ~ 8 have the brightness (L value and diffuse reflectance) that is higher in comparison to the mica of Comparative Examples 4 ~ 7 and are very clear and bright and gives a high feel of brightness.

[0043] Next, explanation is given on the cosmetic in which the glass flake having the said titania coating film, i.e. the pearlescent pigment is blended. Evaluation of the cosmetic was conducted by 5 steps of evaluation by senses of 10 panellers based on [Table 7] below.

[0044] [Table 7]

Evaluation by senses on the cosmetic

Evaluation/ Item	Spreading	Feel of close fit	Smoothness	Feel of brightness	Beauty of color
1	poor	absent	absent	absent	dirty
2	somewhat poor	somewhat absent	somewhat absent	not much present	somewhat lackluster
3	ordinary	ordinary	ordinary	somewhat present	ordinary
4	somewhat good	somewhat present	somewhat present	present	beautiful
5	good	much present	much present	very high	very beautiful

[0045] The result of evaluation by senses is the average value of the 5 steps evaluation by 10 panellers and, to facilitate the understanding of the evaluation, the result of evaluation is expressed by the following codes.

Double circle ---	4.5 ~ 5.0
O -----	3.5 ~ 4.5
• -----	2.5 ~ 3.5
Δ -----	1.5 ~ 2.5
x -----	1.0 ~ 1.5

[0046] (Example of Application 9) Powder foundation

The powder foundation consisting of the materials shown in [Table 8 below] was prepared.

[0047] [Table 8]

(1) Titanium oxide	7
(2) Talcum	20
(3) White mica	3
(4) Glass flake of Example of Application 2	55
(5) Nylon powder	2
(6) Red colored iron oxide	0.5
(7) Yellow colored iron oxide	1
(8) Black colored iron oxide	0.1
(9) Silicone oil	1
(10) 2- ethyl hexyl palmitate	9
(11) Sorbitan sesqui oleate	1
(12) Preservative	0.3
(13) Perfume	0.1 (wt %)

[0048] The materials (1) ~ (8) shown above were mixed by a Henshell mixer. To this mixture, the mixture obtained by melt-heating and mixing the materials (9) ~ (13) shown above was added and mixed and this was pulverized by using a pulverizer. Further, this was discharged into a dish of diameter 5.3 mm and pressure- molded under a pressure of 160 kg/ cm<sup>2</sup> to make the powder foundation. Results of the evaluation by senses of this cosmetic are shown in [Table 9] below.

[0049] (Comparative Example 8) : Powder foundation

The material (4) shown above, i.e. the glass flake, was substituted with the mica of Comparative Example 1. Other than this, the same procedure as in Example of Application 9 was followed to make the powder foundation. Results of evaluation by senses of this cosmetic are shown in [Table 9] below.

[0050] (Comparative Example 9): Powder foundation

The material (4) shown above, i.e. glass flake, was substituted with the glass flake of Comparative Example 3. Other than this, the same procedure as in Example of Application 9 were followed to make the powder foundation. Results of the evaluation by senses of this cosmetic are shown in [Table 9] below together.

[0051] [Table 9]

Item	Spreading	Feel of close fit	Smoothness	Feel of brightness	Beauty of color
EA 9	O	O	O	Double circle	Double circle
CE 8	O	O	O	O	O
CE 9	•	•	Δ	O	Double circle

EA. Example of Application; CE. Comparative Example

[0052] From [Table 9], it is seen that, in comparison to Comparative Example 8, the cosmetic of Example of Application 9 is superior in terms of the feel of brightness and beauty of color and, in comparison to Comparative Example 9, it is superior in terms of the feel of close fit and smoothness.

[0053] (Example of Application 10) Brusher

The brusher that consists of the material shown in Table 10 was prepared.

[0054] [Table 10]

(1) Talcum	12.6
(2) Silk mica	8.1
(3) Mica	25.4
(4) Glass flake of EA 3	45.0
(5) Red Color No. 226	0.4
(6) Squalane	3.0
(7) 2-ethyl hexyl palmitate	5.0
(8) Preservative	0.3
(9) Perfume	0.2 (wt %)

[0055] The materials (1) ~ (5) shown above were mixed with a Henshell mixer. To this mixture, the mixture obtained by heat-melting and mixing the materials (6) ~ (9) shown above was mixed by spraying. Next, this was pulverized by using a pulverizer. Next, this was discharged into a dish of 4 x 6 cm and pressure molded under 129 kg/cm<sup>2</sup> to make the brusher. The results of evaluation by senses of this cosmetic are shown in [Table 11] below.

[0056] (Comparative Example 10): Brusher

The material (4) of Example of Application 10, i.e. glass flake, was substituted with the mica of Comparative Example 2. Other than this, the same procedure of Example of

Application 10 was followed to make the brusher. Results of evaluation by senses of this cosmetic are shown in [Table 11] below.

[0057] (Comparative Example 11): Brusher

The material (4) of Example of Application 10, i.e. glass flake, was substituted with the glass flake of Comparative Example 3. Other than this, the same procedure as in Example of Application 10 was followed to make the brusher. Results of evaluation by senses of this cosmetic are shown in [Table 11] below together.

[0058] [Table 11]

Item	Spreading	Feel of close fit	Smoothness	Feel of brightness	Beauty of color
EA 10	O	O	O	Double circle	Double circle
CE 10	O	O	O	O	O
CE 11	•	•	Δ	O	double circle

EA. Example of Application; CE. Comparative Example

[0059] From [Table 11], it is seen that, in comparison to Comparative Example 10, the cosmetic of Example of Application 10 is superior in terms of the feel of brightness and beauty of color and, in comparison to Comparative Example 11, it is superior in terms of the feel of close fit, smoothness and feel of brightness.

[0060] (Example of Application 11): Nail enamel

Nail enamel consisting of the materials shown in [Table 12] was made.

[0061] [Table 12]

(1) Nitro cellulose	12
(2) Modified alkyd resin	12
(3) Acetyl tri butyl citrate	5
(4) n-butyl acetate	36.4
(5) Ethyl acetate	6
(6) n-butyl alcohol	2
(7) Toluene	21
(8) Iron oxide pigment	0.5
(9) Titanium dioxide	0.1
(10) Glass flake of Example of Application 7	3
(11) Mica	1
(12) Organic modified montmorillonite	1 (wt %)

[0062] The materials (1) ~ (7) shown above (but, only a part of the material (4)) were dissolved and, to this solution, mixture of the material (12) and the remainder of the material (4) in gel form was added and mixed. Then, further, the materials (8) ~ (11) were

added and mixed. This mixture was filled in a prescribed container to make the nail enamel. Results of evaluation by senses of this cosmetic are shown in [Table 13] below.

[0063] (Comparative Example 12): Nail enamel

The material (10) of Example of Application 11, i.e. glass flake, was substituted with the mica of Comparative Example 6. Other than this, the same procedure as that of Example of Application 11 was followed to make the nail enamel. Results of evaluation by senses of this cosmetic are shown in [Table 13] below.

[0064] (Comparative Example 13): Nail enamel

The material (10) of Example of Application 11, i.e. glass flake, was substituted with the glass flake of Comparative Example 3. Other than this, the same procedure as that of Example of Application 11 was followed to make the nail enamel. Results of evaluation by senses of this cosmetic are shown in [Table 13] below.

[0065] [Table 13]

Item	Spreading	Feel of close fit	Smoothness	Feel of brightness	Beauty of color
EA 11	O	O	Double circle	Double circle	Double circle
CE 12	O	O	O	O	O
CE 13	•	•	Δ	O	Double circle

EA. Example of Application; CE. Comparative Example

[0066]

From [Table 13], it is seen that, in comparison to Comparative Example 12, the cosmetic of Example of Application 11 is superior in terms of smoothness, the feel of brightness and beauty of color and, in comparison to Comparative Example 13, it is superior in terms of spreading, the feel of close fit, smoothness and feel of brightness.

[0067] (Example of Application 12): Emulsified foundation

The emulsified foundation consisting of them materials shown in [Table 14] below was prepared.

[0068] [Table 14]

(1) Stearic acid	0.4
(2) Iso stearic acid	0.3
(3) Cetyl 2-ethyl hexanoate	4
(4) Fluid paraffin	11
(5) Poly oxy ethylene (10) stearyl ether	2
(6) Talcum	8
(7) Pigment	4
(8) Cetyl alcohol	0.3

(9) Preservative	0.07
(10) Glass flake of Example of Application 6	10
(11) Tri ethanol amine	0.42
(12) Propylene glycol	5
(13) Preservative	0.02
(14) Ion exchanged water	54.19
(15) Perfume	0.3 (wt %)

[0069] The materials (1) ~ (9) described above were dissolved at 85 deg C and mixed and, to this, the material (10) described above was added and dispersed uniformly. To this, the mixture obtained by dissolving the materials (11) ~ (14) described above at 85 deg C and mixing them was added slowly and emulsified. The temperature at the time of emulsification was maintained for 10 minutes and stirring was done. After this, cooling was done down to 45 deg C while stirring. To this, the material (15) was added and stirring and cooling were continued until 35 deg C. Next, this was filled in a container to obtain the emulsified foundation. Results of evaluation by senses of this cosmetic are shown in [Table 15] below.

[0070] (Comparative Example 14): Emulsified foundation

The material (10) of Example of Application 12, i.e. glass flake, was substituted with the mica of Comparative Example 5. Other than this, the same procedure as that of Example of Application 12 was followed to make the emulsified foundation. Results of evaluation by senses of this cosmetic are shown in [Table 15] below.

[0071] (Comparative Example 15): Emulsified foundation

The material (10) of Example of Application 12, i.e. glass flake, was substituted with the glass flake of Comparative Example 3. Other than this, the same procedure as that of Example of Application 12 was followed to make the emulsified foundation. Results of evaluation by senses of this cosmetic are shown in [table 15] below together.

[0072] [Table 15]

Item	Spreading	Feel of close fit	Smoothness	Feel of brightness	Beauty of color
EA 12	O	O	Double circle	Double circle	Double circle
CE 14	O	O	O	O	Δ
CE 15	•	•	Δ	O	Double circle

EA. Example of Application; CE. Comparative Example

[0073]

From [Table 15], it is seen that, in comparison to Comparative Example 14, the cosmetic of Example of Application 12 is superior in terms of smoothness, the feel of brightness and beauty of color and, in comparison to Comparative Example 15, it is superior in terms of spreading, the feel of close fit, smoothness and feel of brightness.

[0074] (Example of Application 13): Rouge

The rouge consisting of the materials shown in [Table 16] below was made.

[0075] [Table 16]

(1) Hydrocarbon wax	20
(2) Canderila wax	3
(3) Glyceryl iso stearate	40
(4) Fluid paraffin	26.8
(5) Titanium dioxide	4
(6) Glass flake of Example of Application 7	4
(7) Organic pigment	2
(8) Perfume	0.2
	(wt %)

[0076] The materials (1) ~ (4) described above were heat-melted at 85 deg C and, to this, (5) ~ (7) were added and stir-mixed. Next, (8) was mixed and stirred and, next, it was filled in a prescribed container to make the rouge. Results of evaluation by senses of this cosmetic are shown in (Table 17) below.

[0077] (Comparative Example 16): Rouge

The material (6) of Example of Application 13, i.e. glass flake, was substituted with the mica of Comparative Example 6. Other than this, the same procedure as that of Example of Application 13 was followed to make the rouge. Results of evaluation by senses of this cosmetic are shown in [Table 17] below.

[0078] (Comparative Example 17): Rouge

The material (6) of Example of Application 13, i.e. glass flake, was substituted with the glass flake of Comparative Example 3. Other than this, the same procedure as that of Example of Application 13 was followed to make the rouge. Results of evaluation by senses of this cosmetic are shown in [Table 17] below together.

[0079] [Table 17]

Item	Spreading	Feel of close fit	Smoothness	Feel of brightness	Beauty of color
EA 13	O	O	Double circle	Double circle	Double circle
CE 16	O	O	O	O	O
CE 17	•	•	Δ	O	Double circle

EA. Example of Application; CE. Comparative Example

[0080] From [Table 17], it is seen that, in comparison to Comparative Example 16, the cosmetic of Example of Application 13 is superior in terms of smoothness, the feel of brightness and beauty of color and, in comparison to Comparative Example 17, it is superior in terms of spreading, the feel of close fit, smoothness and feel of brightness.

[0081] (Example of Application 14): Eye shadow

The eye shadow consisting of the materials shown in [Table 18] below was made.

[0082] [Table 18]

(1) Talcum	21
(2) White mica	20
(3) Glass flake of Example of Application 8	40
(4) Pigment	12
(5) Squallane	4
(6) Cetyl 2- ethyl hexanoate	1.9
(7) Sorbitan sesquiolate	0.8
(8) Preservative	0.1
(9) Perfume	0.2
	(wt %)

[0083] The materials (1) ~ (4) described above were mixed by a Henshell mixer. To this, the mixture obtained by heat- mixing (5) ~ (9) was mixed by spraying. Next it was pulverized. This was discharged into a prescribed dish to obtain the eye shadow. Results of evaluation by senses of this cosmetic are shown in [Table 19] below.

[0084] (Comparative Example 18): Eye shadow

The material (3) of Example of Application 14, i.e. glass flake, was substituted with the mica of Comparative Example 7. Other than this, the same procedure as that of Example of Application 14 was followed to make the eye shadow. Results of evaluation by senses of this cosmetic are shown in [Table 19] below.

[0085] (Comparative Example 19): Eye shadow

The material (3) of Example of Application 14, i.e. glass flake, was substituted with the glass flake of Comparative Example 3. Other than this, the same procedure as that of Example of Application 14 was followed to make the eye shadow. Results of evaluation by senses of this cosmetic are shown in [Table 19] below.

[0086] [Table 19]

Item	Spreading	Feel of close fit	Smoothness	Feel of brightness	Beauty of color
EA 14	Double circle	Double circle	Double circle	Double circle	Double circle
CE 18	O	O	O	O	O
CE 19	•	•	Δ	O	Double circle

EA. Example of Application; CE. Comparative Example

[0087] From [Table 19], it is seen that, in comparison to Comparative Example 18, the cosmetic of Example of Application 14 is superior in terms of spreading, feel of close fit,

smoothness and feel of brightness and, in comparison to Comparative Example 17, it is superior in terms of spreading, the feel of close fit, smoothness and feel of brightness.

[0088]

[Effectiveness of the Invention] This invention is constituted as described above and so it has the following effectiveness. The pearlescent pigment of the invention described in Claim 1 can provide inexpensive pearlescent pigment having the following characteristics: it has an average thickness of 0.1 ~ 2.5  $\mu\text{m}$ , average particle size of 1 ~ 300  $\mu\text{m}$  and an aspect ratio of 10 ~ 500 and the base material is the glass flake containing silica by 45 ~ 75 wt % and having smooth surface. Further, it is the pearlescent pigment in which the surface of base material is film-coated with metal oxide like titanium oxide and so it does not have lackluster as a cosmetic material and it expresses very good feel of brightness and it does not give the feel of roughness on the skin and has excellent spreading and feel of fit.

[0089] According to the pearlescent pigment of the invention described in Claim 2, precious metal and titania are attached to the surface of base material in addition to the effect of the invention of Claim 1 and, consequently, the titania film of rutile type that is dense and stable is formed by heating at a temperature below 600 deg C.

[0090] The cosmetic of the invention described in Claim 3 uses this pearlescent pigment as the cosmetic material and so it can provide a cosmetic that has a good spreading and excellent feel of fit on the skin and does not generate the feel of roughness and has the beauty of coloring with excellent feel of brightness.

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## Optical Effect Materials

Engelhard Reflecks™ Gilded Gold G232L, Reflecks™ Blazing Bronze G270L, Reflecks™ Clearly Copper G370L and Reflecks™ Really Rouge G670L are novel optical effect materials composed of Calcium Sodium Borosilicate (and) Titanium Dioxide (and) Iron Oxides. These products and their product family typically consist of iron and/or titanium oxide films encapsulating Calcium Sodium Borosilicate platelets. They could potentially be used in a broad range of cosmetic applications, including color cosmetics and personal care. Attached are a number of formulations demonstrating the use of Reflecks™ colors. These examples are not meant to be limiting in any way, and one skilled in the art will readily find many other applications.

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## Liquid Foundation CLF-010240

Phase	Ingredients	% wt.
A.	Xanthan Gum (Keltrol T) <sup>1</sup>	0.20
	Cellulose Gum (CMC 7LF) <sup>2</sup>	0.20
	Water	(q.s. to 100%)
		68.61
B.	Triethanolamine (TEA 99%) <sup>3</sup>	0.65
	PEG-7 Glyceryl Cocoate (Cetiol HE) <sup>4</sup>	6.00
	Methylparaben	0.30
C.	Talc	0.75
	Iron Oxides	1.20
	Reflecks™ Blazing Bronze G270L (Calcium Sodium Borosilicate (and) Iron Oxides) <sup>6</sup>	5.69
D.	Isopropyl Myristate	2.00
	Oleyl Alcohol (Novol) <sup>5</sup>	6.50
	Mineral Oil (and) Lanolin Alcohol (Amerchol L-101) <sup>3</sup>	4.50
	Cetearyl Alcohol (Lanette O) <sup>4</sup>	2.00
	Stearic Acid	1.00
	Propylparaben	0.10
	Imidazolidinyl Urea	0.30
		100.00

### PROCEDURE:

- I. Disperse gums into water using high shear mixing until smooth.
- II. Add Phase B to Phase A and mix until smooth.
- III. Pulverize Phase C and add to Phase A-B using high shear mixing until smooth.
- IV. In a support vessel heat Phase D ingredients to  $75 \pm 5^{\circ}\text{C}$  with gentle agitation.
- V. Add Phase D to Phase A-B-C- with gentle agitation, maintaining temperature at  $75 \pm 5^{\circ}\text{C}$ .
- VI. Maintain constant agitation and cool batch to  $35 \pm 5^{\circ}\text{C}$ ; store or fill into appropriate containers.

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3. Dow Chemical Company
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**CLF-010240**

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## Hair Gel CLH-010238

Phase	Ingredients	% wt.
A.	Water Carbomer (Carbopol Ultrez 10) <sup>1</sup>	(q.s. to 100%) 78.20 0.50
B.	Propylene Glycol Propylene Glycol (and) Diazolidinyl Urea (and) Methylparaben (and) Propylparaben (Germaben II) <sup>2</sup>	4.00 1.00
C.	Triethanolamine	0.50
D.	Water PVP Disodium EDTA Benzophenone-4 (Uvinul MS-40) <sup>3</sup>	15.00 0.20 0.05 0.05
E.	Polysorbate 20 (Tween 20) <sup>4</sup> Fragrance (CK TYPE#18567H) <sup>5</sup> Reflecks™ Blazing Bronze G270L (Calcium Sodium Borosilicate (and) Iron Oxides) <sup>6</sup>	0.20 0.10 0.20 <hr/> 100.00

### PROCEDURE:

- I. Combine Phase A ingredients and mix until thoroughly dispersed.
- II. Add pre-mixed Phase B to Phase A while mixing until completely uniform.
- III. Add Phase C to Phase A-B while under agitation.
- IV. Pre-mix Phase D until ingredients are dissolved and add to Phase A-B-C.
- V. Add pre-mixed Phase E ingredients to Phase A-B-C-D.

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## Gel Cologne CLT-010237

Phase	Ingredients	% wt.
A.	Water Acrylates/C10-30 Alkyl Acrylate Crosspolymer (Carbopol ETD 2020) <sup>1</sup> (2% aqueous dispersion)	25.80
	2-Amino 2-Methyl Propanol (AMP-95) <sup>2</sup>	0.10
B.	Fragrance (Amarige 19434V) <sup>3</sup> Octoxynol-9 (Triton X-100 Surfactant) <sup>4</sup> Butylene Glycol PPG-20 Methyl Glucose Ether (Glucam P-20) <sup>4</sup>	4.00 2.00 1.00 1.00
C.	Alcohol SD-39C <b>Reflecks™ Blazing Bronze G270L</b> (Calcium Sodium Borosilicate (and) Iron Oxides) <sup>5</sup>	56.00 0.10 100.00

### PROCEDURE:

- I. Combine Carbopol ETD 2020 2% aqueous dispersion with water at room temperature and mix until uniform.
- II. Add AMP with mixing. Avoid aeration.
- III. Pre-mix Phase B ingredients.
- IV. Pre-mix Phase C ingredients.
- V. Combine Phase B and C and add to Phase A. Continue to mix until uniform. Avoid aeration

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## Pressed Powder Eye Shadow CLE-010236

Phase	Ingredients	%wt.
A.	Mearltaic TCA® (Talc (and) Lauroyl Lysine) <sup>1</sup> Mearlmica® SVA (Mica (and) Lauroyl Lysine) <sup>1</sup> Magnesium Myristate Silica (Spherica P-1500) <sup>2</sup> <b>Reflecks™ Blazing Bronze G270L</b> (Calcium Sodium Borosilicate (and) Iron Oxides) <sup>1</sup> Propylparaben Imidazolidinyl Urea Methylparaben	17.40 20.00 5.00 2.00 37.00 0.10 0.20 0.20
B.	Octyl Palmitate (Ceraphyl 368) <sup>3</sup> Isostearyl Neopentanoate (Ceraphyl 375) <sup>3</sup> Butylated Hydroxytoluene (BHT)	7.00 1.00 0.10
C.	<b>Reflecks™ Blazing Bronze G270L</b> (Calcium Sodium Borosilicate (and) Iron Oxides) <sup>1</sup>	<u>10.00</u>
		<u>100.00</u>

### PROCEDURE:

- I. Thoroughly blend and disperse Phase A in appropriate dry blending/dispersing equipment.
- II. Add Phase B ingredients into a support vessel. Heat and mix until uniform.
- III. Spray Phase B into premixed Phase A and continue blending.
- IV. Pulverize and return to blender.
- V. Add Phase C to Phase A-B and mix until uniform.

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3. ISP

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## Nail Enamel CLN-010239

Phase	Ingredients	% wt.
A.	Suspending Lacquer SLF-2 (Butyl Acetate (and) Toluene (and) Nitrocellulose (and) Tosylamide/Formaldehyde Resin (and) Isopropyl Alcohol (and) Dibutyl Phthalate (and) Ethyl Acetate (and) Camphor (and) n-Butyl Alcohol (and) Silica (and) Quaterinum-18 Hectorite <sup>1</sup>	82.00
	Reflecks™ Blazing Bronze G270L (Calcium Sodium Borosilicate (and) Iron Oxides) <sup>1</sup>	3.50
	Red 6 Lake (7.9% Dispersion in Nitrocellulose Base, CB-70)	0.80
	Red 7 Lake (7.9% Dispersion in Nitrocellulose Base, CB-11)	0.40
	Red 34 Lake (7.9% Dispersion in Nitrocellulose Base, CB-91) <sup>2</sup>	0.30
	Dimethicone (Dow Coming 200 50cs. - 1% in Butyl Acetate)	1.00
	Lacquer 127P (Butyl Acetate (and) Toluene (and) Nitrocellulose (and) Tosylamide/Formaldehyde Resin (and) Isopropyl Alcohol (and) Dibutyl Phthalate (and) Ethyl Acetate (and) Camphor (and) n-Butyl Alcohol) <sup>1</sup>	5.00
	Tosylamide/Epoxy Resin <sup>3</sup>	3.00
B.	Thinner*	<u>4.00</u>
		100.00

### \*THINNERS:

Butyl Acetate (Urethane Grade)	36.00
Ethyl Acetate (Urethane Grade)	13.00
Toluene	<u>51.00</u>
	100.00

### **PROCEDURE:**

- I. Combine Phase A ingredients in a vessel fitted with a propeller type mixer and stir until uniform.
- II. Combine Phase B ingredients (thinners) in a secondary vessel and mix well until uniform.
- III. Add Phase B to Phase A while stirring until uniform.

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## Shampoo CLH -010241

Phase	Ingredients	% wt.
A.	Water (q.s. to 100.00%) Panthenol (DL-Panthenol) <sup>1</sup> Methylpropanediol (MP Diol LO) <sup>2</sup> Sodium Laureth Sulfate (Jeelate ES-270) <sup>3</sup> Cocamidopropyl Betaine (Jeeteric Cab-LC) <sup>3</sup>	63.25 0.20 2.00 15.00 5.00
B.	Polysorbate 80 (Tween 80) <sup>4</sup> Fragrance (16148M) <sup>5</sup>	0.20 0.20
C.	Water <b>Reflecks™ Blazing Bronze G270L</b> (Calcium Sodium Borosilicate (and) Iron Oxides) <sup>6</sup> Methylchloroisothiazolinone (and) Methylisothiazolinone (Kathon CG) <sup>7</sup>	5.00 0.10 0.05
D.	Acrylates/Aminoacrylates Copolymer (Structure Plus) <sup>8</sup>	9.00
E.	Citric Acid (25% aqueous solution) (q.s. to pH 6.0 +/- 0.5)	<u>q.s.</u> 100.00

### PROCEDURE

- I. Using moderate propeller agitation, add ingredients from Phase A in the order listed at room temperature. Mix until uniform
- II. Pre-mix Phase B ingredients. Add to Phase A.
- III. Add pre-mixed Phase C ingredients with continuous mixing.
- IV. Add Phase D ingredient with continuous mixing.
- V. Adjust pH with Phase E ingredient.

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4. Uniqema
5. Shaw Mudge & Company
6. **Engelhard Corporation**
7. Rohm and Haas Company, Inc.
8. National Starch & Chemical Company

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## Lipstick CLL-010235

Phase	Ingredients	% wt.
A.	Candelilla Wax	2.75
	Carnauba Wax	1.25
	Beeswax	1.00
	Ceresine Wax	5.90
	Ozokerite Wax	6.75
	Microcrystalline Wax (Multiwax 180W) <sup>1</sup>	1.40
	Oleyl Alcohol (Novol) <sup>2</sup>	3.00
	Isostearyl Palmitate (Jeechem ISP) <sup>3</sup>	7.50
	Isostearyl Isostearate (Schercemol 1818) <sup>4</sup>	5.00
	Caprylic/Capric Triglyceride (Neobee M-5) <sup>5</sup>	5.00
	Bis-Diglycerylpolyalcohol Adipate-2 (Softisan 649) <sup>6</sup>	2.00
	Acetylated Lanolin Alcohol (Acetulan) <sup>7</sup>	2.50
	Sorbitan Tristearate (Crill 35) <sup>2</sup>	2.00
	Aloe Vera (Veragel Lipoid 1:1) <sup>8</sup>	1.00
	Castor Oil (q.s. to 100%)	37.30
	Red 6 Lake	0.25
	Tocopheryl Acetate	0.20
	Butylated Hydroxytoluene (BHT)	0.10
	Phenoxyethanol (and) Isopropylparaben, Isobutylparaben (and) Butylparaben (Liquapar PE) <sup>9</sup>	1.00
B.	Reflecks™ Blazing Bronze G270L (Calcium Sodium Borosilicate (and) Iron Oxides) <sup>10</sup> Coslin™ C-100 (Kaolin) <sup>10</sup>	13.00 1.00
C.	Fragrance (Strawberries & Cream) <sup>11</sup>	0.10 100.00

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**PROCEDURE:**

- I. Weigh all the ingredients in Phase A into a heated vessel and raise temperature to  $85 \pm 3^{\circ}\text{C}$ , stirring until melted and uniform.
- II. Add in Phase B and mix until all the pearl pigment is well dispersed.
- III. Add in Phase C and mix with constant stirring.
- IV. Pour at  $75 \pm 5^{\circ}\text{C}$ .
- V. Mold, cool and flame the lipsticks.

Note: If iron oxide or organic pigments are used, they should first be dispersed in Castor oil; this mixture should then be milled in either a colloid or roller mill.

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## REFLECKS™ GILDED GOLD Product No. G232L

### PRODUCT SPECIFICATIONS & PROPERTIES

**Appearance:** A free-flowing sparkling gold powder.

**Pigment Type:** Platelets of Calcium sodium borosilicate, titanium dioxide, iron oxide.<sup>(1)</sup>

**Proposed INCI Name:** Calcium Sodium Borosilicate (and) Titanium Dioxide (and) Iron Oxides

Chemical Composition:	By Weight	CI No.	CAS No.
Calcium sodium borosilicate	92.0 – 97.0%		65997-17-3
TiO <sub>2</sub>	3.0 – 6.0%	77891	13463-67-7
Fe <sub>2</sub> O <sub>3</sub>	<1.0%	77491	1309-37-1
SnO <sub>2</sub> <sup>(2)</sup>	<1.0%		18282-10-5

<b>Trace Elements:</b> <sup>(3)</sup>	Arsenic	1 ppm Max.
	Lead	10 ppm Max.
	Mercury	1 ppm Max.
	Antimony	2 ppm Max.

**Microorganisms:** 100 organisms per gram max. No Pathogens.

**pH:** 7.0-11.0 (4% aqueous solution).

### TYPICAL PROPERTIES

**Particle Size:**<sup>(4)</sup> D(10%), 43µm      D(50%), 94µm      D(90%), 174µm

**Density:** 2.8 Kg/L      23.3 lbs/gal

**Bulk Density:** 64.6 g/100 cm<sup>3</sup>      10.6 g/in<sup>3</sup>      Approx. 40.3 lbs/ft<sup>3</sup>  
**(ASTM D-716-86)**

**NOTES:**

This proposed specification was developed with limited run data and will be finalized as more products are made.

**Footnotes:**

1. Do not use in the area of the eye.
2. Incidental ingredient, Code of Federal Regulation, Title 21, paragraph 701.3 (e) (1).

3. All of the components in this product met the requirements of 21 CFR Part 73.
4. Particle size results will vary depending on the light scattering instrument used. The values listed (% weight) are based on a volume distribution measurement using a Malvern Mastersizer S.
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WO 02/090448 A2

(54) Title: EFFECT PIGMENTS BASED ON COATED GLASS FLAKES

(57) Abstract: The present invention relates to effect pigments based on thin glass flakes and to a method for the production of such pigments. The resulting pigment can be used in any application for which pearlescent pigments have been heretofore used such as, for example, in plastics, paints, inks, cosmetic formulations, coatings including solvent or waterborne automotive paint systems, powder coatings, inks and agriculture foils.

- 1 -

### Effect Pigments based on coated glass flakes

The present invention relates to effect pigments based on thin glass flakes, to  
a method for the production of such pigments and their use in plastics, paints,  
coatings, powder coatings, inks, printing inks, glasses, ceramic products,  
agriculture foils, and in cosmetic formulations.

Since more than 40 years iridescent luster effects can be achieved using so  
called nacreous or pearlescent pigments. Various alternative techniques have  
been developed to create colour/lustre effects. The most important, economic  
and common way to make these pigments is to coat a platelet shaped carrier  
with high refractive substances like  $TiO_2$ ,  $Fe_2O_3$ ,  $SnO_2$ ,  $ZrO_2$ ,  $Cr_2O_3$  or  
combinations of these or with alternating layers of high and/or low refractivity.

So far the nearly exclusively used carrier is wet ground muscovite mica. It is  
cheap, readily available and easy to cleave into smooth and very thin platelets.  
These can be classified into any desired particle size distribution. Additionally,  
pigments based on mica are very stable towards chemical, mechanical or  
thermal treatment. But there are some disadvantages of mica, since it is a  
natural product and shows inconsistencies from source to source and even  
from batch to batch. This has to be overcome by adjusting the processing  
parameters. Natural mica contains impurities like quartz which makes the  
processing more complicated (abrasion of grinding tools, waste) or like Fe, Mn,  
Cu which makes the masstone yellowish grey rather than white. When ground  
it yields platelets showing a broad distribution of thicknesses and diameters.  
This can be reduced by proper classification but will never lead to uniform  
shape.

In the past researchers tried to find corresponding alternatives to mica which  
keep the advantages of it but did not contain the above mentioned  
disadvantages.

- 2 -

A wide variety of other platy materials have been proposed as substitute for mica in the patent literature. These include non-soluble inorganic materials such as glass, enamel, china clay, porcelain, natural stones or other silicaceous substances, metal objects and surfaces of organic polymer materials such as polycarbonate as disclosed for example in U.S. Patents 5 3,123,485, 3,219,734, 3,616,100, 3,444,987, 4,552,593 and 4,735,869. While glass has been mentioned as a possibility on many occasions, for instance in U.S. Patent 3,331,699, commercial pearlescent products are not made using 10 glass and experience has shown that products made using glass as the platelet substrate have rather poor quality.

U.S. Patent 3,331,699 discloses that glass flakes may be coated with a translucent layer of particles of a metal oxide having a high index of refraction, 15 such as titanium dioxide, provided there is first deposited on the glass flakes a nucleating substance which is insoluble in the acidic solution from which the translucent layer of metal oxide is deposited. The patent does not mention the necessity of a smooth transparent film, not particles, being necessary for 20 quality interference pigments to be developed. The patent teaches that the nature of the glass is not critical, but that the presence of the nucleated surface is critical. It is further stated that there are only a small number of 25 metal oxide compounds which are insoluble in the acidic solution and capable of forming a nucleated surface on the glass flakes; tin oxide and a fibrous boehmite form of alumina monohydrate are the only two such materials disclosed. As demonstrated in the examples below, products prepared according to the teachings of this patent are poor in quality.

30 U.S. Patent 5,436,077 teaches a glass flake substrate which has a metal covering layer on which is formed a dense protective covering layer of a metal oxide such as titanium dioxide. In this patent, the nature of the glass is unimportant, the metallic coating provides the desired appearance and the overcoating of the metal oxide is present to protect the metallic layer from 35 corrosive environments.

- 3 -

EP 0 912 640 B1 teaches the coating of thick flakes of C glass having a first coating comprising iron oxide or rutile titanium dioxide thereon. The disadvantage of C glass is the limited thermal stability. As disclosed in the EP 0 912 640 B1 the rutile pigments prepared according to the corresponding examples were calcined at temperatures not higher than 600 °C. It is well known that the calcining temperature is of essential importance for the stability of rutile pigments, especially for outdoor applications. To yield sufficiently stabilized rutile TiO<sub>2</sub> layers on a substrate calcining temperatures of at least 800 °C are requested.

10

For the preparation of pearlescent pigments the transparency and the thickness of the platy substrate are very important. For the first time EP 0 289 240 B1 discloses the manufacturing of extremely thin glass flakes at reasonable costs. According to the claimed process the glass flakes cannot be only made in any desired composition, e. g., from pure SiO<sub>2</sub>, but also in any thickness tailored for the application wanted down to below 0.8 µm.

20

It is an object of the present invention to overcome the problems of the prior art and to provide novel effect pigments which have advantageous application properties. This object is achieved by the inventive effect pigments based on very thin glass flakes having the following characteristics:

25

- (1) thickness of the glass flakes  $\leq$  1.0 µm
- (2) high temperature and mechanical stability
- (3) smooth surfaces

30

The present invention relates to effect pigments based on glass flakes with a thickness of  $\leq$  1.0 µm coated with one or more layers with a high and/or a low reflective index. The thickness of the glass flakes is preferably  $\leq$  0.8 µm and especially  $\leq$  0.5 µm. Especially preferred are thin glass flakes with a softening point  $\geq$  800 °C.

35

Glass can be classified for example as A glass, C glass, E glass, ECR glass.

- 4 -

- For the present invention quartz glass is preferred but the production of this glass is very expensive. Glass types which fulfill the feature of the requested softening point are quartz glass, and any other glass composition having a softening point of  $\geq 800$  °C. Glass flakes which fulfill the requirements are
- 5 special glasses like e. g. Schott Duran or Supremax types. The softening point in the present invention is defined, according to ASTM C 338 as the temperature at which a uniform fiber of glass with a diameter of 0.55-0.75 mm and a length of 23.5 cm increases its length by 1 mm/min when the upper
- 10 10 cm is heated at a rate of 5 °C/min.
- Suitable glass flakes preferably prepared according to EP 0 289 240 B1 are characterized in that they contain an average particle size in the range of 5 - 1000  $\mu\text{m}$ , preferably in the range of 5-150  $\mu\text{m}$ . Preferred glass flakes have an
- 15 average particle size in the range of 5-150  $\mu\text{m}$  and a thickness of 0.1-0.5  $\mu\text{m}$ , preferably of 0.1-0.3  $\mu\text{m}$ . The aspect ratio of glass flakes is in the range of 10-300, preferably in the range of 50-200.
- The glass particles can be coated with one or more layers selected from the group consisting of metal oxides, metal suboxides, metal fluorides, metal oxyhalides, metals chalcogenides, metal nitrides, metal sulfides, metal carbides, or mixtures thereof.
- 20 Examples of suitable metal oxides are  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiFe}_2\text{O}_5$ , Ti suboxides,  $\text{Fe}_3\text{O}_4$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{ZnO}$ ,  $\text{SnO}_2$ ,  $\text{CoO}$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{VO}_2$ ,  $\text{V}_2\text{O}_3$ ,  $\text{Sn}(\text{Sb})\text{O}_2$  or mixtures thereof. The  $\text{TiO}_2$  layer can be in the rutile or anatase modification, preferably the  $\text{TiO}_2$  layer is rutile. Especially preferred are glass
- 25 30 flakes coated with  $\text{TiO}_2$  and/or  $\text{Fe}_2\text{O}_3$ .
- Metal sulfide coatings on glass flakes are preferably selected from sulfides of tin, silver, lanthanum, rare earth metals, preferably cerium, chromium, molybdenum, tungsten, iron, cobalt and/or nickel.
- 35 The glass flakes can be coated in the same way as e. g. mica based pearl lustre pigments. Coatings with a metal oxide may be accomplished by any

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known methods, such as hydrolysis of a metal salt by heating or alkali, which deposits hydrated metal oxide, optionally followed by calcination.

5 In general, the procedure involves the dispersing of the thin glass flake particles and combining that dispersion with a precursor which forms a hydrous metal oxide film coating on the flakes.

10 After the glass is dispersed in water and placed in an appropriate vessel, the appropriate metal salts are added. The pH of the resulting dispersion is maintained at an appropriate level during the addition of the metal salts by simultaneous feeding a suitable base, for example sodium hydroxide, to cause precipitation of the hydrous metal dioxide on the glass flakes. An aqueous acid, for example hydrochloric acid, can be used for adjusting the pH. The  
15 coated platelets can, if desired, be washed and dried before being calcined to the final pigment. The procedure is described in detail in U.S. Patent 5,433,779 and in the German Patents 14 67 468, 19 59 998, 20 09 566, 22 14 545, 22 15 191, 22 44 298, 23 13 331, 25 22 572, 31 37 808, 31 37 809,  
20 31 51 343, 31 51 354, 31 51 355, 32 11 602 and 32 53 017.

25 The effect pigments of the present invention are preferably prepared by wet-chemically coating of the glass flakes or by gas phase decomposition of volatile metal compounds (CVD, PVD) or electroless plating.

The effect pigments obtained in this way are characterized in that one or more homogeneous layers enrobing the uniform thin glass flakes.

30 Preferred effect pigments of the present invention are given in the following:  
glass flake + TiO<sub>2</sub> (rutile)  
glass flake + Fe<sub>2</sub>O<sub>3</sub>  
glass flake + Fe<sub>3</sub>O<sub>4</sub>  
35 glass flake + TiFe<sub>2</sub>O<sub>5</sub>  
glass flake + Cr<sub>2</sub>O<sub>3</sub>  
glass flake + ZrO<sub>2</sub>

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- glass flake + Sn(Sb)O<sub>2</sub>  
glass flake + BiOCl  
glass flake + Al<sub>2</sub>O<sub>3</sub>  
glass flake + Ce<sub>2</sub>S<sub>3</sub>  
5 glass flake + MoS<sub>2</sub>

In general, the layer thickness ranges from 0.1 to 1000 nm, preferably from 0.2 to 300 nm. The optical layer thickness will in general be adapted to the particular application. Preferred pigments are coated with one or two layers.

10

To enhance the light and weather stability it is frequently advisable, depending on the field of application, to subject the coated glass flakes to a surface treatment. Useful surface treatments include for example the processes 15 described in DE-C 22 15 191, DE-A 31 51 354, DE-A 32 35 017 or DE-A 33 34 598, DE 40 30 727 A1, EP 0 649 886 A2, WO 97/29059, WO 99/57204, U.S. 5,759,255. This surface treatment further enhances the chemical stability of the pigments and/or facilitates the handling of the pigment, especially its incorporation into various application media.

20

The effect pigments of the present invention are advantageous useful for many purposes, such as the coloring of plastics, glasses, ceramic products, agriculture foils, decorative cosmetic formulations and in particular coatings, 25 especially automotive coatings, and inks, including printing inks. All customary printing processes can be employed, for example offset printing, intaglio printing, bronze printing, flexographic printing. Furthermore they can be used as functional pigments like conductive pigments, as magnetic pigments or to make media, for example plastics, board products and papers, laser-markable.

30

The effect pigments of the present invention are also advantageously useful for these applications in admixture with filler pigments or transparent and hiding white, colored and black organic and inorganic pigments and also with conventional transparent, colored and black luster pigments based on metal oxide coated mica, TiO<sub>2</sub> flakes, SiO<sub>2</sub> flakes or Al<sub>2</sub>O<sub>3</sub> flakes and coated or

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uncoated metal pigments, BiOCl pigments, platelet shaped iron oxides, or graphite flakes.

5 Additionally, the inventive pigment mixtures can contain organic or inorganic colourants, thixotropy agents, wetting agents, dispersing agents, water, organic solvent or solvent mixtures, etc.

10 The pigment mixtures of the invention are simple and easy to handle. The pigment mixtures can be incorporated into the system in which it is used by simple mixing. Laborious milling and dispersing procedures for the pigments are not necessary.

15 The coated glass flakes of the invention can be used for pigmenting and/or coating materials, printing inks, plastics, agricultural films, button pastes, for the coating of seed, for the colouring of food, coatings of foods, medicaments or cosmetic formulations. The concentration of the pigments in the system in which it is to be used for pigmenting is generally between 0.01 and 50 % by weight, preferably between 0.1 and 5 % by weight, based on the overall solids content of the system. This concentration is generally dependent on the specific application.

25 Plastics comprising the pigment mixture of the invention in amounts of 0.1 to 50 % by weight, in particular from 0.5 to 7 % by weight, are frequently notable for a particular brilliance.

30 In the coating sector, especially in automotive finishing, the glass flakes are employed in amounts of 0.5 to 10 % by weight.

35 In the pigmentation of binder systems, for example for paints and printing inks for intaglio, offset or screen printing, the pigment is incorporated into the printing ink in amounts of 2 - 50 % by weight, preferably 5 - 30 % by weight and in particular 8 - 15 % by weight.

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The invention likewise provides pigment preparations comprising coated glass flakes, optionally effect pigments, binders and, if desired, additives, the said preparations being in the form of substantially solvent-free, free-flowing granules. Such granules contain up to 95 % by weight of the inventive pigments. A pigment preparation in which the glass flakes of the invention are pasted up with a binder and with water and/or an organic solvent, with or without additives, and the paste is subsequently dried and brought into a compact particulate form, e. g. granules, pellets, briquettes, a masterbatch or tablets, is particularly suitable as a precursor for printing inks.

10

The present invention therefore also provides formulations containing the pigments of the invention.

15 In order to further illustrate the invention, various non-limiting examples are set forth below. In these, as well as throughout the balance of this specification and claims, all parts and percentages are by weight and all temperatures are in degrees centigrade unless otherwise indicated.

20

### Examples

#### Example 1 (Rutile Silver pigment) Prior Art

25 200 g flakes of E-glass (thickness: 5 µm; diameter: 10-40 µm; specific surface area: approximately 0.2 m<sup>2</sup>/g) are suspended in 2 l of deionized water. With vigorous stirring the suspension is heated to 80 °C. After having adjusted the pH to 2.0 with dilute HCl a first layer of SnO<sub>2</sub> is precipitated onto the glass flakes by feeding a solution of 3 g SnCl<sub>4</sub> x 5 H<sub>2</sub>O (in 10 ml conc. HCl plus 30 50 ml of DI water) into the suspension under simultaneous neutralization with 10 % NaOH over a period of about 1 h. To complete the reaction the suspension is kept stirring for another 15 min. The coating is continued by adjusting the pH to 1.8 with dilute HCl and then titrating 63.5 ml of 35 TiCl<sub>4</sub>-solution (400 g TiCl<sub>4</sub>/l DI water) against 10 % NaOH over a period of about 3 h. Having reached the desired layer thickness the coating is stopped,

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stirred for another 15 min, filtered, washed with DI water and dried. After calcination at 800 °C for 30 min a silverwhite rutile pigment is yielded.

5       Example 2 (Rutile Silver pigment)

200 g flakes of E-glass (thickness: 0.5 µm; diameter: 10-40 µm; specific surface area: approximately 1.7 m<sup>2</sup>/g) are suspended in 2 l of DI water. The coating is carried out the same way as in example 1. Titration periods keep the  
10      same, only the amounts of solutions are adjusted to the different base material:

- 5 g SnCl<sub>4</sub> x 5 H<sub>2</sub>O (in 15 ml conc. HCl plus 75 ml DI water)  
196.3 ml of TiCl<sub>4</sub> solution (400 g TiCl<sub>4</sub>/l DI water)  
15      After calcination at 800 °C for 30 min a brilliant silverwhite rutile pigment is yielded.

20       Examples 3 and 4 (Rutile Interference Green pigment)

The coatings are started in the same ways as for examples 1 and 2, only the amount of TiO<sub>2</sub> (400 g TiCl<sub>4</sub>/l DI water) coated was increased to yield green interference type pigments. The further steps are again carried out as  
25      described in examples 1 and 2.

- To evaluate their properties draw down cards are made from all of these pigments. Additionally sprayed panels were prepared.  
30      The pigments based on glass flakes with a thickness of 5.0 µm and 0.5 mm are checked for their coloristics and their visual performance.

35       Results:

- draw downcards and panels pigments with a thickness of 5.0 µm showed

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very weak performance making a "dilute" impression. For the silver little brilliance and little hiding effect was observed while for the green a dull colour and little brilliance are found;

- a little better is the effect in the sunlight as some larger flakes show a kind of sparkle;
- completely different is the situation with a thickness of 0.5 mm pigments: They exceeded comparable mica pigments regarding brilliance, lustre and (for the green) chroma;
- particularly impressing is the high transparency combined with clear color;
- looking with the microscope shows that the surfaces of all pigments are well and uniformly coated and that the differences result mostly from the imperfect orientation of the 5 mm particles;

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### Claims

1. Effect pigments based on glass flakes with a thickness of  $\leq 1.0 \mu\text{m}$  characterized in that the glass flakes are coated with one or more layers with a high and/or low refractive index.  
5
2. Effect pigments according to claim 1, characterized in that the softening point of the glass flakes is  $\geq 800^\circ\text{C}$ .
- 10 3. Effect pigments according to claim 1 or 2, characterized in that the glass flakes are coated with one or more layers of metal oxides, metal suboxides, metal oxyhalides, metal fluorides, metal chalcogenides, metal nitrides, metal sulfides, metal carbides, or mixtures thereof.
- 15 4. Effect pigments according to claim 3, characterized in that the metal oxide is  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiFe}_2\text{O}_5$ , Ti suboxides,  $\text{Fe}_3\text{O}_4$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{ZnO}$ ,  $\text{SnO}_2$ ,  $\text{CoO}$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{VO}_2$ ,  $\text{V}_2\text{O}_3$ ,  $\text{Sn}(\text{Sb})\text{O}_2$  or mixtures thereof.
- 20 5. Effect pigments according to claim 4, characterized in that the glass flakes are coated with  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$  or a mixture of  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$ .
- 25 6. Effect pigments according to claim 4 or claim 5, characterized in that the  $\text{TiO}_2$  is in the rutile modification.
7. Effect pigments according to claim 3, characterized in that the coatings are metal sulfides selected from sulfides of tin, silver, lanthanum, rare earth metals, chromium, molybdenum, tungsten, iron, cobalt and/or nickel.  
30
8. Effect pigments according to any of the claims 1 to 7, characterized in that the glass flakes are coated with one or two layers.  
35
9. A method of preparing an effect pigment according to claim 1 which

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comprises coating of the glass flakes by wet chemical coating, by chemical or physical vapor deposition or electroless plating and optionally calcining the coated glass flakes.

- 5      10. Use of the effect pigments according to claim 1 in plastics, coatings, powder coatings, paints, inks, printing inks, glasses, ceramic products, agriculture foils and in cosmetic formulations.
- 10     11. Use of the effect pigments according to claim 1 as conductive pigments, as magnetic pigments or as dopants for the laser-marking of papers and plastics.
- 15     12. Formulations containing the effect pigments according to claim 1.

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(54) Title: MULTILAYER PIGMENTS BASED ON GLASS FLAKES

(57) Abstract: The present invention relates to multilayer pigments based on glass flakes and to a method for the production of such pigments. The resulting pigment can be used in any application for which pearlescent pigments have been heretofore used such as, for example, in plastics, paints, inks, cosmetic formulations, coatings including solvent or waterborne automotive paint systems, powder coatings, inks and agriculture foils, for the laser-marking of papers and plastics.

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### Multilayer pigments based on glass flakes

- The present invention relates to multilayer pigments based on glass flakes, to a method for the production of such pigments and their use in plastics, paints, coatings, powder coatings, inks, printing inks, glasses, ceramic products, agriculture foils, for laser-marking of papers and plastics and in cosmetic formulations.
- Lustre pigments or special-effect pigments are employed in numerous fields in industry, especially in the sector of automotive finishes, in decorative coatings, in plastics, in paints, in printing inks and in cosmetic formulations.
- Multilayer interference pigments with alternating layers of high and low refractive index are known. They differ in respect of the carrier material and of the material of the individual layers, and in the preparation process. The layers are prepared either by precipitation in a wet process or by vapor deposition or sputtering under vacuum. The layers applied to the carrier or to a release layer are all optically active and contribute to the development of the interference colors.
- U.S.P. 4,434,010 discloses a multilayer interference pigment consisting of a central layer of a reflective metal, such as aluminum, and alternating layers of two transparent dielectric materials of high and low refractive index respectively, such as titanium dioxide and silicon dioxide, for example. This multilayer pigment is used preferably for counterfeit-protected products like securities or banknotes.
- JP H7-759 discloses a multilayer interference pigment with metallic lustre, for which a substrate is coated with alternate layers of titanium dioxide and silicon dioxide. The substrate comprises flakes of aluminum, gold or silver, or of mica or glass, with a coating of metals. The depth effect which is

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characteristic of and desired for interference pigments, however, cannot be generated. This is because of the total reflection of the light at the metal layer which forms the core. Consequently, the interference effect remains limited to the layers which are located on top of the metal layer.

5 Furthermore, the lack of transparency of the substrate greatly restricts options for combinations with further pigments in applications-related formulations.

10 U.S.P. 3,438,796 and U.S.P. 5,135,812 describe, for example, metal lustre pigments having a central essentially non-transparent aluminum film coated on both sides in alternation with dielectric films of low refractive index, such as silicon dioxide or magnesium fluoride, and with partially transparent metal films, such as films of chromium or aluminum, for  
15 example. Owing to the preparation process, the central metal film of these pigments is coated only on the top and bottom sides of the platelets, while the side areas constitute broken edges and lie open towards the medium.

20 DE 44 05 494, DE 44 37 753, DE 195 16 181 and DE 195 15 988 disclose lustre pigments prepared by coating metal platelets, especially aluminum flakes, with metal oxide layers of low refractive index, such as with a silicon dioxide layer, and with non-selectively absorbing metal oxide layers or  
25 metal layers of high refractive index, using CVD or wet chemical techniques.

30 Lustre pigments based on metal substrates frequently have good properties, including good hiding, but the result on application, such as in the paint, for example, is a "hard" metallic lustre, which is frequently undesired.

35 Lustre pigments based on transparent platelet-shaped substrates which do not have this "hard" metallic lustre are the subject of WO 93/12182. Mica flakes are covered with a metal oxide layer of high refractive index,

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such as TiO<sub>2</sub>, and with a nonselectively absorbing layer. Depending on the thickness of the TiO<sub>2</sub> layer, when viewed straight on these pigments exhibit a particular interference colour which becomes increasingly weaker as the viewing angle becomes more oblique and which finally flips to gray or black. The interference color does not change, but a decrease is found in the color saturation.

JP 1992/93206 claims lustre pigments on the basis of glass flakes or mica particles which are covered with a reflecting metal layer and with alternating layers of SiO<sub>2</sub> and TiO<sub>2</sub>.

EP 0 753 545 A2 discloses lustre pigments based on multiply coated, non-metallic, platelet-shaped substrates which are of high refractive index and which are at least partially transparent to visible light and have at least one layer assembly comprising a colorless coating of low refractive index and a reflective coating which absorbs selectively or nonselectively.

Disadvantages of this invention are the technically very complex and costly preparation process and the frequent difficulty in reproducing the pigments in the desired product quality.

U.S.P. 3,331,699 discloses that glass flakes may be coated with a translucent layer of particles of metal oxide having a high index of refraction, such as titanium dioxide, provided there is first deposited on the glass flakes a nucleating substance which is insoluble in the acidic solution from which the translucent layer of metal oxide is deposited. The patent does not mention that smooth transparent films, not particles, are necessary for quality interference pigments to be developed. The patent teaches that the nature of the glass is not critical, but that the presence of the nucleated surface is critical. It is further stated that there are only a small number of metal oxide compounds which are insoluble in the acidic solution and capable of forming a nucleated surface on the glass flakes; tin

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oxide and a fibrous boehmite form of alumina monohydrate are the only two such materials disclosed. As demonstrated in the examples below, products prepared according to the teachings of this patent are poor in quality.

5

U.S. Patent 5,436,077 teaches a glass flake substrate which has a metal covering layer on which is formed a dense protective covering layer of a metal oxide such as titanium dioxide. In this patent, the nature of the glass is unimportant, the metallic coating provides the desired appearance and  
10 the overcoating of the metal oxide is present to protect the metallic layer from corrosive environments.

15

For the preparation of pearlescent pigments the transparency and the thickness of the platy substrate are very important. For the first time EP 0 289 240 B1 discloses the manufacturing of extremely thin glass flakes at reasonable costs. According to the claimed process the glass flakes can be made in any desired composition, e. g., from pure SiO<sub>2</sub> and also in any thickness tailored for the intended application down to below  
20 1.0 µm.

25

It is an object of the present invention to overcome the problems of the prior art and to provide novel multilayer pigments which have  
advantageous application properties.

30

Surprisingly, an interference pigment has now been found which is based on multiply coated glass flakes and comprises a particular arrangement of optically functional layers by means of which particular optical effects are achieved.

35

The invention therefore provides interference pigments on the basis of multiply coated glass flakes which contain at least three alternating layers with a high and a low refractive index.

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Preferably the layer structure is as of follows:

- (A) a coating having a refractive index  $n > 1.8$ ,
  - 5 (B) a coating having a refractive index  $n \leq 1.8$ , and
  - (C) a coating having a high refractive index  $n > 1.8$
- and, if desired,
- 10 (D) an outer protective layer.

The invention also provides the pigments of the invention for the use in  
15 paints, lacquers, printing inks, plastics, agricultural foils, ceramic materials,  
glasses and cosmetic formulations and for the use in laser-marking of  
papers and plastics.

20 Preferred glass flakes have a thickness of less than 1  $\mu\text{m}$ , preferably  $< 0.8$   
 $\mu\text{m}$ . Especially preferred are glass flakes with a thickness of  $\leq 0.5 \mu\text{m}$ .  
Glass can be classified for example as A glass, C glass, E glass, ECR  
glass. For the present invention quartz glass is preferred but this glass is  
very expensive.

25 Suitable glass flakes preferably prepared according to EP 0 289 240 B1  
are characterized in that they contain an average particle size in the range  
of 5 - 1000  $\mu\text{m}$ , preferably in the range of 5 – 150  $\mu\text{m}$ . Preferred glass  
30 flakes have an average particle size in the range of 5 - 150  $\mu\text{m}$  and a  
thickness of 0.1 - 0.8  $\mu\text{m}$ , preferably of 0.2 – 0.5  $\mu\text{m}$ . The aspect ratio of  
glass flakes is in the range of 10 – 300, preferably in the range of 50 - 200.

35 The glass flakes can be coated in the same way as conventional pearl  
lustre pigments. Coatings with a metal oxide may be accomplished by any

- 6 -

known methods, such as hydrolysis of a metal salt by heating or under  
alkaline conditions, which deposits hydrated metal oxide, followed by  
calcination. In general, the procedure involves the dispersing of the thin  
glass flake particles and combining that dispersion with a precursor which  
5 forms a hydrous metal oxide film coating on the flakes.

The thickness of the individual layers of high and low refractive index on  
the base substrate is essential for the optical properties of the pigment. For  
10 a pigment with intensive interference colors, the thickness of the individual  
layers must be adjusted precisely with respect to one another.

If  $n$  is the refractive index of a thin layer and  $d$  its thickness, the  
interference colour of this layer is defined by the product  $n \cdot d$  ( $n \cdot d =$   
15 optical thickness). The colors which result from such a film under  
perpendicular light incidence in reflected light result from an intensification  
of the light of wavelength

$$20 \quad \lambda = \frac{4}{2N-1} \cdot n \cdot d$$

and by an attenuation of the light of wavelength

$$25 \quad \lambda = \frac{2}{N} \cdot n \cdot d$$

where  $N$  is a positive integer.

30 The variation in color which results with increasing film thickness is a  
consequence of the intensification or attenuation of certain light  
wavelengths through interference. If two or more layers in a multilayer  
pigment possess the same optical thickness, the color of the reflected light  
35 becomes more intense as the number of layers increases. In addition,

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it is possible through an appropriate choice of layer thickness to achieve a particularly strong variation of color as a function of the viewing angle. A pronounced, so-called color flop is developed. The thickness of the individual layers, preferably metal oxide layers, irrespective of their refractive index, depends on the field of use and is generally from 10 to 5 1000 nm, preferably from 15 to 800 nm and, in particular, 20 to 600 nm.

The multilayer pigments of the invention preferably feature a coating (A) of high refractive index in combination with a colorless coating (B) of low 10 refractive index and located thereon a coating of high refractive index. The pigments can comprise two or more, identical or different combinations of layer assemblies, although preference is given to covering the substrate with only one layer assembly (A) + (B) + (C). In order to make the color flop 15 more intense the pigment of the invention may comprise up to 4 layer assemblies, although the thickness of the combined layers on the substrate should not exceed 3  $\mu\text{m}$ .

20 The glass particles can be coated with three or more layers, preferably with 3, 4, 5, 6 or 7 layers from the group consisting of metal oxides, metal suboxides, metal fluorides, metal oxyhalides, metal sulfides, metal chalcogenides, metal nitrides, metal oxynitrides, metal carbides, or mixtures thereof. Especially preferred are glass flakes coated with 3, 5 or 7 25 layers. The layer packet (A) and (B) may be present in the standard layer assembly (A) + (B) + (C) up to four times.

30 The layer (A) of high refractive index has a refractive index  $n > 1.8$ , preferably  $n \geq 2.1$ . Materials suitable as the layer material (A) are all materials known to the skilled worker which are of high refractive index, are filmlike and can be applied homogeneously to the substrate particles. Particularly suitable materials are metal oxides, metal sulfides or metal 35 oxide mixtures, such as  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiFe}_2\text{O}_5$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{BiOCl}$ ,  $\text{CoO}$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{VO}_2$ ,  $\text{V}_2\text{O}_3$ ,  $\text{Sn}(\text{Sb})\text{O}_2$ ,  $\text{ZrO}_2$ ,  $\text{ZnO}$  or  $\text{SnO}_2$ , iron titanates, iron oxide

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hydrates, titanium suboxides (reduced titanium species having oxidation states from < 4 to 2) bismuth vanadate, cobalt aluminate, and also mixtures or mixed phases of these compounds with one another or with other metal oxides.

5

Metal sulfide coatings are preferably selected from sulfides of tin, silver, lanthanum, rare earth metals, preferably cerium, chromium, molybdenum, tungsten, iron, cobalt and/or nickel.

10

The thickness of the layer (A) is 10 – 550 nm, preferably 15 – 400 nm and, in particular, 20 – 350 nm.

Colorless materials of low refractive index suitable for the coating (B) are  
15 preferably metal oxides or the corresponding oxide hydrates, such as  $\text{SiO}_2$ ,  $\text{MgF}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{AlO(OH)}$ ,  $\text{B}_2\text{O}_3$  or a mixture of these metal oxides. The thickness of the layer (B) is 10 – 1000 nm, preferably 20 – 800 nm and, in particular 30 – 600 nm.

20

Materials particularly suitable for the coating (C) of high refractive index are colorless or colored metal oxides such as  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiFe}_2\text{O}_5$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{BiOCl}$ ,  $\text{CoO}$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{VO}_2$ ,  $\text{V}_2\text{O}_3$ ,  $\text{Sn(Sb)}\text{O}_2$ ,  $\text{ZrO}_2$ ,  $\text{ZnO}$  or  $\text{SnO}_2$ , iron titanates, iron oxide hydrates, titanium suboxides, bismuth vanadate, cobalt

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aluminate, and also mixtures or mixed phases of these compounds with one another or with other metal oxides. The  $\text{TiO}_2$  layers additionally can contain absorbing material, e.g. carbon, or coated therewith. Also of particular interest are multiply coated glass flakes whose  $\text{TiO}_2$  coating (C)

30

is partially reduced and which as well as unchanged  $\text{TiO}_2$  contains reduced titanium species having oxidation states from < 4 to 2 (lower oxides as  $\text{Ti}_3\text{O}_5$ ,  $\text{Ti}_2\text{O}_3$  through  $\text{TiO}$ , titanium oxynitrides and also titanium nitride). It is also possible to use colorless high refractive materials, for example metal

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oxides such as zirconium dioxide, in particular titanium dioxide, which have been colored with selectively absorbing colorants, by incorporation of

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colorants in the metal oxide layer, by doping thereof with selectively absorbing metal cations or by coating the metal oxide layer with a colorant like for example prussian blue or carmine. The thickness of the layer (C) is 10 – 550 nm, preferably 15 – 400 nm and, in particular, 20 – 350 nm.

5        In addition to the standard layer packet (A) + (B) + (C), in which the layer packet of (A) + (B) may be present up to four times in the pigment of the invention, there are other preferred embodiments. For instance, between the substrate (S) and the layer (A), between the layer (A) and (B), between  
10      layer (B) and (C) and/or between layer (C) and the top layer (D) the pigment of the invention may have a further absorbing or nonabsorbing layer [(S1), (A1), (B1), (C1)]. The thickness of the interlayers is 1 – 50 nm, preferably 1 – 40 nm and, in particular, 1- 30 nm. The inventive pigments  
15      may contain a plurality of identical or different combinations (layer packets) of (A) + (B).

20      The multilayer coated glass flakes obtained in this way are characterised in that at least three homogeneous layers are surrounding the uniform thin glass flakes.

25      Preferred effect pigments of the present invention are given in the following:

	glass flakes	+	TiO <sub>2</sub>	+	SiO <sub>2</sub>	+	TiO <sub>2</sub>
	glass flakes	+	TiO <sub>2</sub>	+	SiO <sub>2</sub>	+	Fe <sub>2</sub> O <sub>3</sub>
	glass flakes	+	TiO <sub>2</sub>	+	SiO <sub>2</sub>	+	TiO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub>
30	glass flakes	+	TiO <sub>2</sub>	+	SiO <sub>2</sub>	+	(Sn,Sb)O <sub>2</sub>
	glass flakes	+	(Sn,Sb)O <sub>2</sub>	+	SiO <sub>2</sub>	+	TiO <sub>2</sub>
	glass flakes	+	Fe <sub>2</sub> O <sub>3</sub>	+	SiO <sub>2</sub>	+	(Sn,Sb)O <sub>2</sub>
	glass flakes	+	TiO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub>	+	SiO <sub>2</sub>	+	TiO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub>
35	glass flakes	+	TiO <sub>2</sub>	+	SiO <sub>2</sub>	+	MoS <sub>2</sub>

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	glass flakes	+ TiO <sub>2</sub>	+ SiO <sub>2</sub>	+ Cr <sub>2</sub> O <sub>3</sub>
	glass flakes	+ Cr <sub>2</sub> O <sub>3</sub>	+ SiO <sub>2</sub>	+ TiO <sub>2</sub>
	glass flakes	+ Fe <sub>2</sub> O <sub>3</sub>	+ SiO <sub>2</sub>	+ TiO <sub>2</sub>
	glass flakes	+ TiO <sub>2</sub>	+ Al <sub>2</sub> O <sub>3</sub>	+ TiO <sub>2</sub>
5	glass flakes	+ Fe <sub>2</sub> TiO <sub>5</sub>	+ SiO <sub>2</sub>	+ TiO <sub>2</sub>
	glass flakes	+ TiO <sub>2</sub>	+ SiO <sub>2</sub>	+ Fe <sub>2</sub> TiO <sub>5</sub> /TiO <sub>2</sub>
	glass flakes	+ TiO suboxides	+ SiO <sub>2</sub>	+ TiO <sub>2</sub> suboxides
	glass flakes	+ TiO <sub>2</sub>	+ SiO <sub>2</sub>	+ TiO <sub>2</sub> +SiO <sub>2</sub> +TiO <sub>2</sub> + Prussian Blue
10	glass flakes	+ TiO <sub>2</sub>	+ SiO <sub>2</sub>	+ TiO <sub>2</sub> + SiO <sub>2</sub> + TiO <sub>2</sub>
	glass flakes	+ TiO <sub>2</sub> +SiO <sub>2</sub> +TiO <sub>2</sub>	+ SiO <sub>2</sub>	+ TiO <sub>2</sub> + SiO <sub>2</sub> + TiO <sub>2</sub>

and if desired,

(D) an outer protective layer.

15

A particularly preferred embodiment is the coating of the glass flakes with the following layer assembly:

- 20      (S1) optional, SnO<sub>2</sub>
- (A) TiO<sub>2</sub> or Fe<sub>2</sub>O<sub>3</sub>
- (B) SiO<sub>2</sub>
- (B1) optional, SnO<sub>2</sub>
- (C) TiO<sub>2</sub>
- 25      (D) final coating related to application

Coating the substrates with layers (A) and (C) with a high refractive index and, if desired, further colored or colorless coatings produces pigments 30 whose color, gloss, hiding power and angular dependence of perceived color can be varied within wide limits.

The pigments of the invention are easy to produce by virtue of the 35 generation of three or more interference layers of high and low refractive index, precisely defined thickness and smooth surface on the thin glass

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flakes. In case of layers with different metal oxides or metal oxide mixtures the sequences of high refractive index layers in the multilayer stack can be arranged arbitrary as long as a low refractive index layer is present in between.

5

The metal oxide layers are preferably applied by wet-chemical means, it being possible to use the wet-chemical coating techniques developed for the production of pearl lustre pigments; techniques of this kind are described, for example, in DE 14 67 468, DE 19 59 988, DE 20 09 566, 10 DE 22 14 545, DE 22 15 191, DE 22 44 298, DE 23 13 331, DE 25 22 572, DE 31 37 808, DE 31 37 809, DE 31 51 343, DE 31 51 354, DE 31 51 355, DE 32 11 602, DE 32 35 017, DE 38 42 330 or else in further patent documents and other publications.

15

Layers of TiO<sub>2</sub> can be in the rutile or anatase modification. Preferred are TiO<sub>2</sub> (rutile) layers. Titanium dioxide layers can be also reduced by known means, e.g. ammonia, hydrogen, hydrocarbon vapor and mixtures thereof or metal powders, as described in EP 0 735 114, DE 34 33 657, DE 41 25 20 134, EP 0 332 071, EP 0 707 050 or WO 93/19131. Mixed iron oxide/titanium dioxide layers can be made either by subsequent precipitation or by co-precipitation of the individual metal oxides. In the case of wet coating, the substrate particles are suspended in water, and hydrolysable 25 metal salts are added at a pH which is appropriate for hydrolysis and is chosen such that the metal oxides or metal oxide hydrates are precipitated directly onto the platelets without any instances of side precipitation. The pH is kept constant usually by simultaneous metered addition of a base and/or acid. Subsequently, the pigments are filtered off, washed and dried 30 and, if desired, calcined, with the option to adjust the calcination temperature in respect of the particular coating present. In general, the calcination temperatures are between 250 and 1000 °C, preferably between 350 and 900 °C. If desired, the pigments may be calcined before 35 being resuspended for the application of further layers by precipitation.

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Coating can also take place in a fluidized-bed reactor by means of gas-phase coating, in which case it is possible, for example, to make appropriate use of the techniques proposed in EP 0 045 851 and EP 0 106 235 for preparing pearl lustre pigments.

5

The metal oxide of high refractive index used is preferably titanium dioxide and/or iron oxide, and the metal oxide of low refractive index preferably used is silicon dioxide.

10

For the application of the titanium dioxide layers, preference is given to the technique described in US 3,553,001.

15

An aqueous titanium salt solution is added slowly to a suspension of the substrate to be coated, heated to about 50 – 100 °C, and a substantially constant pH of about 0.5 – 5 is maintained by simultaneous metered addition of a base, for example aqueous ammonia solution or aqueous alkali metal hydroxide solution. As soon as the desired layer thickness of the TiO<sub>2</sub> precipitate has been reached, the addition of both titanium salt solution and base is terminated.

20

25

This technique, also referred to as the titration process, is notable for the fact that it avoids an excess of titanium salt. This is achieved by supplying to the hydrolysis only that quantity per unit time which is necessary for uniform coating with the hydrated TiO<sub>2</sub> and which can be received per unit time by the available surface area of the particles to be coated. Hereby, the formation of hydrated titanium dioxide particles not precipitated onto the surface to be coated can be minimized.

30

35

The application of the silicon dioxide layers can be performed, for example, as follows: A potassium or sodium silicate solution is metered into a heated (50-100 °C) suspension of the substrate that is to be coated. The pH is

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held constant at about 6 – 9 by simultaneous addition of a dilute mineral acid, such as HCl, HNO<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>. As soon as the desired layer thickness of SiO<sub>2</sub> has been reached, the addition of the silicate solution is terminated. The suspension is subsequently stirred for about 0.5 h.

- 5        To enhance the light and weather stability it is frequently advisable, depending on the field of application, to subject the multilayer coated glass flakes to a surface treatment. Useful surface treatments and aftertreatments include for example the processes described in DE-C 22  
10      15 191, DE-A 31 51 354, DE-A 32 35 017 or DE-A 33 34 598, DE 40 30 727 A1, EP 0 649 886 A2, WO 97/29059, WO 99/57204, US 5,759,255. This surface treatment further enhances the chemical stability of the pigments and/or facilitates the handling of the pigment, especially its  
15      incorporation into various application media.

Multilayer pigments generated in this way yield optically highly improved effect pigments at comparatively low costs with

- 20      - superior brilliance  
          - clear and intense colors  
          - intense color travel  
          - alternatively high performance optical filter properties  
25      - very good transparency (important in mixed formulations)

and therefore suited for practically all applications known in the field of pigments. At the same time their shape and particle size can be freely  
30      tailored for an optimum performance.

Especially the last mentioned aspect is of high importance as for many applications it is absolutely necessary to adjust the particle shape. For  
35      cosmetic use, it is necessary to reduce the size and the thickness to achieve a smooth and silky appearance. For automotive paints or printing inks it is a

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must to reduce the particle sizes down to below 40 µm or even 20 µm in diameter. This of course means that the thicknesses must follow this trend to maintain an aspect ratio needed for attractive effects. For these examples therefore thicknesses of the substrate of < 0.8 µm and < 0.5 µm are required.

5 The glass flakes made by the above mentioned process fulfill these requirements. Furthermore they show a superior planarity and smoothness (surface microstructure) which can be expressed by the ratio BET (specific surface area) to WCA (water covering area) as described for aluminum pigments in U.S.P. 4,936,913 and U.S.P. 5,127,951. The values are around 3  
10 which indicate the optimum suitability of the material. The high quality of these flakes also explains the observed high transparency of pigments made therefrom.

15 The preferred designs for the inventive multilayer pigments are:  
> 3 - < 40 µm diameter for automotive applications, or even more preferred  
10 – 35 µm, and  
> 0.2 - < 1 µm average thickness, preferred 0.4 – 0.8 µm  
20 > 3 - < 20 µm diameter for printing applications, preferred 5 – 20 µm, and  
> 0.2 - < 0.5 µm average thickness.

25 The effect pigments of the present invention are advantageously useful for many purposes, such as the coloring of plastics, glasses, ceramic products, agricultural foils, decorative cosmetic formulations and in particular coatings, especially automotive coatings, and inks, including printing inks. All customary printing processes can be employed, for example offset printing, intaglio printing, bronzing, flexographic printing.

30 The effect pigments of the present invention are also advantageously useful for these purposes in admixture with filler pigments or transparent and hiding white, colored and black organic and anorganic pigments and also with conventional transparent, colored and black luster pigments  
35 based on metal oxide coated mica, TiO<sub>2</sub> flakes, SiO<sub>2</sub> flakes or Al<sub>2</sub>O<sub>3</sub> flakes

- 15 -

- and coated or uncoated metal pigments, BiOCl pigments, platelet shaped iron oxides, or graphite flakes. The inventive pigments can be further coated with organic or inorganic layers to yield combination pigments.
- 5     Additionally, the inventive pigment mixture can contain organic or inorganic colorants, thixotropic agents, wetting agents, dispersing agents, water, organic solvent or solvent mixtures, etc.
- 10    The pigment mixture of the invention is simple and easy to handle. The pigment mixture can be incorporated into the system in which it is used by simple stirring. Laborious milling and dispersing of the pigments is not necessary.
- 15    The coated glass flakes of the invention can be used for pigmenting and/or coating materials, printing inks, plastics, agricultural films, button pastes, for the coating of seed, for the coloring of food, coatings of medicaments or cosmetic formulations. The concentration of the pigments in the system in which it is to be used is generally between 0.01 and 50 % by weight, preferably between 0.1 and 5 % by weight, based on the overall solids content of the system. This concentration is generally dependent on the specific application.
- 20    Plastics comprising the pigment mixture of the invention in amounts of 0.1 to 50 % by weight, in particular from 0.5 to 7 % by weight, are frequently notable for a particular brilliance.
- 25    In the coating sector, especially in automotive finishing, the pigments according to the invention are employed in amounts of 0.5 to 10 % by weight.
- 30    In the pigmentation of binder systems, for example for paints and printing inks for intaglio, offset or screen printing, the pigment is incorporated into
- 35

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the printing ink in amounts of 2 - 50 % by weight, preferably 5 - 30 % by weight and in particular 8 - 15 % by weight.

5       The invention likewise provides pigment preparations comprising multilayer coated glass flakes, optionally effect pigments, binders and, if desired, additives, said preparations being in the form of substantially solvent-free, free-flowing powders or granules. Such granules contain up to 95 % by weight of the inventive pigments. A pigment preparation in which the multilayer coated glass flakes of the invention are pasted up with a binder  
10      and with water and/or an organic solvent, with or without additives, and in which the paste is subsequently dried and brought into a compact particulate form, e.g. granules, pellets, briquettes, a masterbatch or tablets, is particularly suitable as a precursor for printing inks.

15      The present invention therefore also provides formulations containing the pigments of the invention.

20      In order to further illustrate the invention, various non-limiting examples are set forth below. In these, as well as throughout the balance of this specification and claims, all parts and percentages are by weight and all temperatures are in degrees centigrade unless otherwise indicated.

25      Examples

Example 1

30      100 g glass flakes with a maximum diameter of 40 µm (average 22 µm) and an average thickness of 0.5 µm (refractive index 1.5) are suspended in 2 l deionized water. Under vigorous stirring the slurry is heated to 75 °C and the coating is started by feeding an aqueous solution of SnCl<sub>4</sub> representing an amount of 3 % of SnO<sub>2</sub> relative to the glass flakes within  
35

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0.5 h. As soon as pH 2,0 is reached 32 % NaOH solution is simultaneously fed in to keep the pH at this value.

5       The slurry is kept stirring for 15 min before the feeding of aqueous TiCl<sub>4</sub> solution (400 g TiCl<sub>4</sub>/l H<sub>2</sub>O) is started. The pH is kept constant at 2.0 with NaOH. It is continued until the desired colour is achieved. The slurry is kept stirring for again 15 min.

10      By slowly adding NaOH the pH is raised to 8.0 before the feeding of 1,35 ml/min of 10% sodium silicate solution (from 74 ml of sodium silicate solution with 8 % Na and 27 % SiO<sub>2</sub> diluted with 170 ml of deionized water) is started. The amount necessary for a proper layer thickness has to be exactly calculated because it is not optically visible during the coating process. After again stirring for 15 min the pH is lowered with 10 % HCl to 2.0 and the second coating of TiO<sub>2</sub> is carried out like the first one until the desired end point is reached. The slurry is kept stirring for one more hour, then filtered off, washed free from salts, dried, calcined at 800 °C ( for 30 minutes ) and sieved.

20      From the pigment yielded a draw down is made to measure the coloristic properties. It shows a highly brilliant clear color effect combined with a superior transparency. Especially in the shallow observation angle of the black background it nearly "disappears".

25

Example 2 (comparative example)

30      This is carried out in the same way like Example 1. Instead of glass flakes mica of the same particle size distribution is used.

The effect on the draw down of the finished pigment is brilliant and color intense but it does not exhibit the unique clearness and particularly the transparency in the shallow angle shown by the glass flakes based multilayer pigments.

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Example 3

- 100 g glass flakes with a maximum diameter of 40 µm (average 22 µm) and an average thickness of 0.8 µm (refractive index 1.5) are suspended in  
5 2 l of deionized water. The suspension is heated to 75 °C, adjusted to a pH of 1.8 with dilute hydrochloric acid, first of all coated with SnO<sub>2</sub> by adding 3.3 ml/min of SnCl<sub>4</sub> solution (from 2.2 g of SnCl<sub>4</sub> and 7.5 ml of conc. hydrochloric acid in 100 ml of deionized water). The pH is held constant using 32 % sodium hydroxide solution.  
10 Stirring is continued for 15 minutes and then coating with TiO<sub>2</sub> is carried out under the same pH/temperature conditions by adding 1.5 ml/min of TiCl<sub>4</sub> solution (400 g of TiCl<sub>4</sub>/l) and keeping the pH constant with 32 % sodium hydroxide solution. Coating is interrupted after the second-order green end point is reached, stirring is continued for 15 minutes, the pH is adjusted to 8.0 with diluted sodium hydroxide solution (over the course of about 15 minutes), and then stirring is continued for 10 minutes more.  
15 Coating with SiO<sub>2</sub> is then carried out by adding 3 ml/min of dilute sodium silicate solution (from 7.3 g of sodium silicate solution with 8 % Na and 27 % SiO<sub>2</sub> and 80 ml of deionized water) without pH compensation. Afterwards, stirring is continued for 15 minutes, the pH is readjusted to 1.8  
20 with dilute hydrochloric acid (over the course of about 10 minutes) and a second TiO<sub>2</sub> layer is applied as described above by adding TiCl<sub>4</sub> solution. Coating is interrupted after the third-order green comparison end point has been reached, stirring is continued for 15 minutes, and then the pigment is  
25 filtered off, washed, dried and calcined at 850 °C for 30 minutes.  
30

The pigment obtained has an intense green interference color. The division of the TiO<sub>2</sub> layers is as follows:

- 19 -

1 <sup>st</sup> layer:	about 170 nm
2 <sup>nd</sup> layer:	about 85 nm
Total layer:	about 260 nm.

- 5        The thickness of the SiO<sub>2</sub> interlayer is about 5 nm.

Example 4

- 10      100 g glass flakes with a maximum diameter of 40 µm (average 22 µm) and an average thickness of 0.5 µm (refractive index 1.5) are suspended in 2 l of deionized water. The suspension is heated to 75 °C, adjusted to a pH of 1.8 with dilute hydrochloric acid, first of all coated with SnO<sub>2</sub> by adding 3.3 ml/min of SnCl<sub>4</sub> solution (from 2.2 g of SnCl<sub>4</sub> and 7.5 ml of conc. hydrochloric acid in 100 ml of deionized water). The pH is held constant using 32 % sodium hydroxide solution.

20      Stirring is continued for 15 min., the pH is adjusted to 2.6 with 32 % sodium hydroxide solution and an Al<sub>2</sub>O<sub>3</sub>/Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> layer is applied by adding 1 ml/min TiCl<sub>4</sub>/FeCl<sub>3</sub>/AlCl<sub>3</sub> solution (394 ml from 165 g 30 % TiCl<sub>4</sub> solution, 274 g, 34 % FeCl<sub>3</sub> solution, 6.2 g AlCl<sub>3</sub> x 6 H<sub>2</sub>O and 63 ml deionized water).

25      Stirring is continued for 15 min., the pH is adjusted to 7.5 with 1.3 ml/min 32 % sodium hydroxide and then stirring is continued for 15 min. more. Coating with SiO<sub>2</sub> is carried out by adding 2 ml/min sodium silicate solution with 13.5 % SiO<sub>2</sub> (from 196 g sodium silicate solution with 27 % SiO<sub>2</sub> and 196 ml deionized water). The pH is held constant using 15 % hydrochloric acid.

30      Stirring is continued for 30 min., the pH is adjusted to 1.8 by adding 1 ml/min of SnCl<sub>4</sub> solution (from 3 g of SnCl<sub>4</sub>, 10 ml of conc. hydrochloric acid and 90 ml deionized water).

- 20 -

Stirring is continued for 15 min., pH is adjusted to 2.6 with 32 % sodium hydroxide solution and a second  $\text{TiO}_2/\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$  layer is applied by adding 1 ml/min  $\text{TiCl}_4/\text{FeCl}_3/\text{AlCl}_3$  solution (394 ml of the same composition as first layer). The stirring is continued for another 15 min and then the pigment is filtered off, washed, dried and calcined at 850 °C for 30 min.

5

The pigment obtained shows a brilliant and intense gold interference color.

Example 5

10

100 g glass flakes with a maximum diameter of 40  $\mu\text{m}$  (average 22  $\mu\text{m}$ ) and an average thickness of 0.5  $\mu\text{m}$  (refractive index 1.5) are suspended in 2 l of deionized water. The suspension is heated to 75 °C, adjusted to a pH of 1.8 with dilute hydrochloric acid, first of all coated with  $\text{SnO}_2$  by adding 3.3 ml/min of  $\text{SnCl}_4$  solution (from 2.2 g of  $\text{SnCl}_4$  and 7.5 ml of conc. hydrochloric acid in 100 ml of deionized water). The pH is held constant using 32 % sodium hydroxide solution.

15

Stirring is continued for 15 min and then coating with  $\text{TiO}_2$  is carried out under the same pH/temperature conditions by adding 1 ml/min  $\text{TiCl}_4$  solution (15 ml with 400 g  $\text{TiCl}_4/\text{l}$ ) and keeping the pH constant with 32 % sodium chloride solution.

20

Stirring is continued for 15 min., the pH is adjusted to 2.6 with 32 % sodium hydroxide solution and an  $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3/\text{TiO}_2$  layer is applied by adding 1 ml/min  $\text{TiCl}_4/\text{FeCl}_3/\text{AlCl}_3$  solution 376 ml from 157.5 g 30 %  $\text{TiCl}_4$  solution, 236 g 34 %  $\text{FeCl}_3$  solution, 5.9 g  $\text{AlCl}_3 \times 6 \text{H}_2\text{O}$  and 60 ml deionized water).

25

30

Stirring is continued for 15 min., the pH is adjusted to 7.5 with 1.3 ml/min 32 % sodium hydroxide and then stirring is continued for 15 min more.

35

Coating with  $\text{SiO}_2$  is carried out by adding 2 ml/min sodium silicate solution

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with 13.5 % SiO<sub>2</sub> (from 196 g sodium silicate solution with 27 % SiO<sub>2</sub> and 196 ml deionized water). The pH is held constant using 15 % hydrochloric acid.

5      Stirring is continued for 30 min., the pH is adjusted to 1.8 by adding 1 ml/min of SnCl<sub>4</sub> solution (from 3 g of SnCl<sub>4</sub>, 10 ml of conc. hydrochloric acid and 90 ml deionized water).

10     Stirring is continued for 15 min and then the second coating with TiO<sub>2</sub> is carried out under the same pH/temperature conditions by adding 2 ml/min TiCl<sub>4</sub> solution (280 ml with 400 g TiCl<sub>4</sub>/l) and keeping the pH constant with 32 % sodium hydroxide solution.

15     Stirring is continued for 15 min., pH is adjusted to 2.6 with 32 % sodium hydroxide solution and a final TiO<sub>2</sub>/Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> layer is applied by adding 0.8 ml/min TiCl<sub>4</sub>/FeCl<sub>3</sub>/AlCl<sub>3</sub> solution (72 ml of the same composition as the first layer). The stirring is continued for another 15 min. and then the pigment is filtered off, washed, dried and calcined at 850 °C for 30 min.

20     The pigment obtained shows an even more brilliant and intense gold interference color than the pigment according to example 4.

25

### Use Examples

#### Use Example 1: Shimmering Foundation

30

#### Phase A

	Extender W	Mica, CI 77891 (Titanium Dioxide)	9,00 %	(1)
	Microna® Matte Yellow	Mica, CI 77492 (Iron Oxides)	4,00 %	(1)
35	Microna® Matte Red	CI 77491 (Iron Oxides), Mica	0,40 %	(1)

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	Microna® Matte Black	CI 77499 (Iron Oxides), Mica	0,30 % (1)
	Pigment according to Example 1	Silica, CI77891 (Titanium dioxide), Mica, Tin oxide	4,50 % (1)
	Ronasphere®	Silica	5,00 % (1)

5

Phase B

	Blanose 7 HF	Cellulose Gum	0,20 % (2)
	Veegum	Magnesium Aluminium Silicate	1,00 % (3)
10	Texapon K 1296	Sodium Lauryl Sulfate	0,60 % (4)
	Triethanolamine	Triethanolamine	0,50 % (1)
	Titriplex III	Disodium EDTA	0,25 % (1)
	Methyl-4-hydroxybenzoate	Methylparaben	0,15 % (1)
	1,2-Propandiol	Propylene Glycol	10,90 % (1)
15	Water	Aqua (Water)	42,95 %

Phase C

	Isopropyl myristate	Isopropyl Myristate	8,00 % (4)
20	Paraffin	Paraffinum Liquidum (Mineral Oil)	3,60 % (1)
	Crodamol SS	Cetyl Esters	2,60 % (5)
	Monomuls 60-35 C	Hydrogenated Palm Glycerides	1,70 % (4)
	Stearic acid	Stearic Acid	1,50 % (1)
	Eusolex® 6300	4-Methylbenzylidene Camphor	1,30 % (1)
25	Eusolex® 4360	Benzophenone-3	0,50 % (1)
	RonaCare™ Tocopheryl acetate	Tocopheryl Acetate	0,10 % (1)
	Magnesium stearate	Magnesium Stearate	0,10 % (1)
	Propyl-4-hydroxybenzoate	Propylparaben	0,05 % (1)

30      Phase D

	Parfum 200 529	Parfum	0,20 % (6)
	Euxyl K 400	Phenoxyethanol, Methylbromo- Glutaronitrile	0,20 % (7)

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Procedure:

Heat all ingredients of phase C to 75 °C while stirring until everything is melted. Add Blanose and Veegum separately to cold water of phase B under high agitation (Turrax). Heat to 75 °C and add the remaining ingredients of phase B and mix until the mixture is smooth and uniform.

5                   Add ingredients of phase A. At 75 °C incorporate phase C into phase A/B and homogenize for 2 min. Add phase D at 40 °C. Cool down to room temperature while stirring and adjust pH to 6,0 - 6,5 einstellen (e.g. citric acid solution).

10

Supplier:

- (1) Merck KGaA/Rona®
- (2) Aqualon GmbH
- 15                 (3) Vanderbilt
- (4) Cognis GmbH
- (5) Croda GmbH
- (6) Fragrance Resources
- (7) Schülke & Mayr GmbH

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Use Example 2: Shower Gel

25                 Phase A

Pigment according to

Example 1

Keltrol T	Xanthan Gum	0,10 % (1)
Water	Aqua (Water)	0,75 % (2)

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64,95 %

Phase B

Plantacare 2000 UP	Decyl Glucoside	20,00 % (3)
Texapon ASV 50	Sodium Laureth Sulfate, Sodium Laureth-8 Sulfate, Magnesium Laureth Sulfate, Magnesium Laureth-8 Sulfate,	

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	Sodium Oleth Sulfate, Magnesium Oleth Sulfate	3,60 % (3)
Bronidox L	Propylene Glycol, 5-Bromo-5-Nitro-1,3-Dioxane	0,20 % (3)
Parfum Everest 79658 SB	Parfum	0,05 % (4)
1 % FD&C Blue No. 1 in water	Aqua (Water), CI 42090 (FD&C Blue No. 1)	0,20 % (5)
5		

Phase C

	Citric acid monohydrate	Citric Acid	0,15 % (1)
10	Water	Aqua (Water)	10,00 %

Procedure:

15 Disperse the pigment in the water of phase A. Incorporate Keltrol T while stirring and mix until thoroughly dispersed. Add phase B and phase C successively to phase A while stirring and stir slowly until the gel is homogeneous.

Supplier:

- 20 (1) Merck KGaA/Rona®  
 (2) Kelco  
 (3) Cognis GmbH  
 (4) Haarmann & Reimer GmbH  
 25 (5) BASF AG

Use Example 3: Intaglio printing ink

30 Intaglio printing ink consisting of

- 70 g Nitrocellulose-based binder from Gebrüder Schmidt 95 MB 011  
 with a solid content of 20 %  
 15 g Minatec® 31 CM (conductive pigment from Merck KGaA,  
 35 Darmstadt, Germany

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15 g Coated glass flakes according to Example 1

Use Example 4: Plastic

5 1 kg of polyethylene (PE-HD) granules are uniformly wetted in a tumble mixer with 2 g of adhesion agent. Then 10 g coated glass flakes according to Example 4 and 2 g of Iridin LS 825 (conductive pigment from Merck KGaA, Darmstadt, Germany with a particle size < 15 µm are added and the components are mixed for 2 minutes.

10 These granules are processed under conventional conditions on an injection moulding machine to give small stepped plates measuring 4 x 3 x 0.5 cm. The small stepped plates are notable for their lustre and their laser markability.

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Use Example 5: Coating

20 30 g Coated glass flakes according to Example 5  
10 g Minatec® 40 CM (conductive pigment from Merck KGaA, Darmstadt, Germany)  
42 g Paint base (AU-MF system, solids = 19 %)  
18 g Diluent mixture

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### Claims

1. Multilayer pigments based on glass flakes characterized in that the glass flakes are coated with alternating layers with a high and a low refractive index and that the glass flakes are coated with at least three layers.  
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2. Multilayer pigments according to Claim 1, characterized in that the pigments comprise at least one layer sequence comprising  
10 (A) a coating having a refractive index  $n > 1.8$   
(B) a coating having a refractive index  $n \leq 1.8$  and  
(C) a coating having a refractive index  $n > 1.8$ ,  
and if desired,  
15 (D) an outer protective layer

with the proviso that the layer packet (A) + (B) may be present in the standard layer assembly (A) + (B) + (C) up to four times.

- 20 3. Multilayer pigments according to Claim 1 or 2, characterized in that the glass flakes have a thickness of less than  $1 \mu\text{m}$ .
- 25 4. Multilayer pigments according to any of the Claims 1 to 3, characterized in that the layers consist of metal oxides, metal suboxides, metal fluorides, metal oxyhalides, metal chalcogenides, metal sulfides, metal nitrides, metal oxynitrides, metal carbides, or mixtures thereof.
- 30 5. Multilayer pigments according to any of the Claims 1 to 4, characterized in that the layer with a high refractive index consist of  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$   $\text{TiFe}_2\text{O}_5$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{BiOCl}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{ZnO}$ ,  $\text{SnO}_2$ ,  $\text{CoO}$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{VO}_2$ ,  $\text{V}_2\text{O}_3$ , iron titanates, iron oxide hydrates, titanium suboxides, bismuth vanadate, cobalt aluminate, metal sulfides, metal

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chalogenides, metal nitrides, metal oxynitrides, metal carbides, or mixtures thereof.

6. Multilayer pigments according to any of Claims 1 to 5, characterized  
5 in that the layer with a low refractive index consists of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, AlO(OH), B<sub>2</sub>O<sub>3</sub>, MgF<sub>2</sub> or mixtures thereof.
7. Multilayer pigments according to Claim 2, characterized in that they  
10 have the following layer structure:

	glass flakes + TiO <sub>2</sub>	+ SiO <sub>2</sub>	+ TiO <sub>2</sub>
	glass flakes + TiO <sub>2</sub>	+ SiO <sub>2</sub>	+ Fe <sub>2</sub> O <sub>3</sub>
	glass flakes + TiO <sub>2</sub>	+ SiO <sub>2</sub>	+ TiO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub>
15	glass flakes + TiO <sub>2</sub>	+ SiO <sub>2</sub>	+ (Sn,Sb)O <sub>2</sub>
	glass flakes + (Sn,Sb)O <sub>2</sub>	+ SiO <sub>2</sub>	+ TiO <sub>2</sub>
	glass flakes + Fe <sub>2</sub> O <sub>3</sub>	+ SiO <sub>2</sub>	+ (Sn,Sb)O <sub>2</sub>
	glass flakes + TiO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub>	+ SiO <sub>2</sub>	+ TiO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub>
20	glass flakes + TiO <sub>2</sub>	+ SiO <sub>2</sub>	+ MoS <sub>2</sub>
	glass flakes + TiO <sub>2</sub>	+ SiO <sub>2</sub>	+ Cr <sub>2</sub> O <sub>3</sub>
	glass flakes + Cr <sub>2</sub> O <sub>3</sub>	+ SiO <sub>2</sub>	+ TiO <sub>2</sub>
	glass flakes + Fe <sub>2</sub> O <sub>3</sub>	+ SiO <sub>2</sub>	+ TiO <sub>2</sub>
	glass flakes + TiO <sub>2</sub>	+ Al <sub>2</sub> O <sub>3</sub>	+ TiO <sub>2</sub>
25	glass flakes + Fe <sub>2</sub> TiO <sub>5</sub>	+ SiO <sub>2</sub>	+ TiO <sub>2</sub>
	glass flakes + TiO <sub>2</sub>	+ SiO <sub>2</sub>	+ Fe <sub>2</sub> TiO <sub>5</sub> /TiO <sub>2</sub>
	glass flakes + TiO suboxides	+ SiO <sub>2</sub>	+ TiO <sub>2</sub> suboxides
	glass flakes + TiO <sub>2</sub>	+ SiO <sub>2</sub>	+ TiO <sub>2</sub> +SiO <sub>2</sub> +TiO <sub>2</sub> + Prussian Blt
30	glass flakes + TiO <sub>2</sub>	+ SiO <sub>2</sub>	+ TiO <sub>2</sub> + SiO <sub>2</sub> + TiO <sub>2</sub>
	glass flakes + TiO <sub>2</sub> +SiO <sub>2</sub> +T <sub>2</sub>	+ SiO <sub>2</sub>	+ TiO <sub>2</sub> + SiO <sub>2</sub> + TiO <sub>2</sub>

and if desired,

(D) an outer protective layer.

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8. Multilayer pigments according to any of the Claims 1 to 7 characterized in that the glass flakes are coated with three layers.
9. A method of preparing a multilayer pigment which comprises coating of the glass flakes by wet chemical coating, or by chemical or physical vapor deposition and calcining the coated glass flakes.  
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10. Use of the multilayer pigments according to claim 1 in plastics, coatings, powder coatings, paints, inks, printing inks, glasses, ceramic products, agriculture foils, in cosmetic formulations, for the laser-marking of papers and plastics.  
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11. Formulations containing the multilayer pigments according to Claim 1.  
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12. Non-dusting powders, pastes and granules containing multilayer pigments according to Claim 1.

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